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# On the Regularity in the Stark Effect on the Spectral Lines of Hydrogen and Helium

By

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Since Stark's discovery of the effect of an intense electric field on the spectral lines of hydrogen helium and lithium, this effect has been investigated by many experimenters. On the one hand, many positive results were obtained in the spectral lines belonging to the other elements; and on the other, the effect on the spectral lines of hydrogen and helium became very clear in their details. As to the first four Balmer lines of hydrogen, Stark has succeeded in photographing the manner of decomposition in "Feinzerlegung," and obtained a number of components in each of the four lines above-mentioned. His first communication on the "Feinzerlegung" in the electric field of 74000 volts per centimeter is described in his "Electrische Spektral Analyse Chemischer Atome." And a better result obtained by employing the electric field of 104000 volts per centimeter is reported in Ann. d. Phys., Bd. 48, S. 193, 1915. According to this latter communication the manner of decomposition of each of the four lines above mentioned was quite symmetrical in reference to the undisplaced position of the original line. A small displacement of about one Å.U. of the central perpendicular component of $H_\gamma$ toward the red side was observed by T. Takamine and N. Kokubu[1] in a strong electric field of about 130000 volts per centimeter, but this minute dissimilarity is disregarded in the following.

1 Takamine and Kokubu, Mem. Coll. Sci., Kyoto, **3**, 271 (1919).

TABLE I, parallel components.

| Wave length | Term number of the series, m. | $\Delta\lambda$ in A. U. obs. by Stark at $10{\cdot}4\times10^4$ volt/cm. | Difference of $\Delta\lambda$ | $\Delta\nu$ obs. by Stark at $10{\cdot}4\times10^4$ volt/cm. | Difference of $\Delta\nu$ obs. | $p$ | $\Delta\lambda$ calc. at $10{\cdot}4\times10^4$ volt/cm. |
|---|---|---|---|---|---|---|---|
| 6563·1 (Hα) | 3 | 11·5 | 2·7 | 26·7 | 6·3 | 8 | 12·0 |
| | | 8·8 | 2·6 | 20·4 | 6·0 | 7 | 9·0 |
| | | 6·2 | — | 14·4 | | 6 | 6·0 |
| | | — | — | | | 5 | 3·0 |
| | | | | | | 4 | 0·0 |
| 4861·6 (Hβ) | 4 | 19·4 | 3·0 | 82·0 | 12·6 | 8 | 19·8 |
| | | 16·4 | 3·2 | 69·4 | 13·5 | 7 | 16·6 |
| | | 13·2 | 3·2 | 55·9 | 13·6 | 6 | 13·2 |
| | | 10·0 | 3·3 | 42·3 | 14·0 | 5 | 9·9 |
| | | 6·7 | 3·4 | 28·3 | 14·3 | 4 | 6·6 |
| | | 3·3 | 3·3 | 14·0 | 14·0 | 3 | 3·3 |
| | | 0·0 | | 0·0 | | 2 | 0·0 |
| 4340·5 (Hγ) | 5 | 29·4 | | 156 | | 9 | 30·4 |
| | | — | 5·5 | | 29 | 8 | 26·4 |
| | | 23·9 | 4·0 | 127 | 21·1 | 7 | 22·4 |
| | | 19·9 | 4·0 | 105·9 | 21·5 | 6 | 18·5 |
| | | 15·9 | 5·3 | 84·4 | 28·1 | 5 | 14·5 |
| | | 10·6 | 4·0 | 56·3 | 21·2 | 4 | 10·6 |
| | | 6·6 | 3·9 | 35·1 | 20·7 | 3 | 6·6 |
| | | 2·7 | | 14·4 | | 2 | 2·6 |
| 4102·0 (Hδ) | 6 | 37·5 | 4·1 | 223 | 24 | 9 | 37·7 |
| | | 33·4 | 4·8 | 199 | 29 | 8 | 33·0 |
| | | 28·6 | 4·4 | 170 | 26 | 7 | 28·3 |
| | | 24·2 | 4·6 | 144 | 27·5 | 6 | 23·6 |
| | | 19·6 | 5·2 | 116·5 | 30·8 | 5 | 18·9 |
| | | 14·4 | 4·8 | 85·7 | 28·6 | 4 | 14·2 |
| | | 9·6 | 4·4 | 57·1 | 26·1 | 3 | 9·4 |
| | | 5·2 | | 31·0 | | 2 | 4·7 |
| | | — | | | | 1 | 0·0 |

TABLE 2, perpendicular components.

| Wave length | Term number of the series, m. | $\Delta\lambda$ obs. in Å. U. at $10{\cdot}4\times10^4$ volt/cm. | Difference of $\Delta\lambda$ | $\Delta\nu$ obs. at $10{\cdot}4\times10^4$ volt/cm. | Difference of $\Delta\nu$ | $p$ | $\Delta\lambda$ calc. at $10{\cdot}4\times10^4$ volt/cm. |
|---|---|---|---|---|---|---|---|
| 6563·1 (Hα) | 3 | 2·6<br>0·0 | 2·6 | 6·2<br>0·0 | 6.2 | 7<br>6 | 3·0<br>0·0 |
| 4861·6 (Hβ) | 4 | 19·3<br>16·4<br>13·2<br>9·7<br>6·6<br>3·4<br>0·0 | 2·9<br>3·2<br>3·5<br>3·1<br>3·2<br>3·4 | 81·8<br>69·4<br>56·0<br>41·0<br>28·0<br>14·4<br>0·0 | 12·4<br>13·4<br>15·0<br>13·0<br>13·6<br>14·4 | 9<br>8<br>7<br>6<br>5<br>4<br>3 | 19·9<br>16·6<br>13·3<br>9·9<br>6·6<br>3·3<br>0·0 |
| 4340·5 (Hγ) | 5 | 26·3<br>22·8<br>—<br>17·3<br>13·3<br>9·7<br>3·9<br>0·0 | 3·5<br>5·5<br>4·0<br>3·6<br>5·8<br>3·9 | 140<br>121<br>92·0<br>70·8<br>51·6<br>20·7<br>0·0 | 19<br>29<br>21.2<br>19·2<br>30·9<br>20·7 | 9<br>8<br>7<br>6<br>5<br>4<br>3<br>2 | 27·7<br>23·7<br>19·8<br>15·8<br>11·9<br>7·9<br>4·0<br>0·0 |
| 4102·0 (Hδ) | 6 | 34·8<br>30·4<br>25·8<br>21·2<br>17·2<br>11·9<br>7·4<br>2·4 | 4·4<br>4·6<br>4·6<br>4·0<br>5·3<br>4·5<br>5·0 | 207<br>181<br>154<br>126<br>106<br>71·0<br>44·0<br>14·3 | 26<br>27<br>28<br>20<br>35<br>27<br>30 | 9<br>8<br>7<br>6<br>5<br>4<br>3<br>2 | 35·4<br>30·6<br>25·9<br>21·2<br>16·5<br>11·8<br>7·1<br>2·4 |

Already from the results in "Grobzerlegung" Stark and others have pointed out that the displacements of the components of Balmer lines were proportional to the strength of the electric field. In the case of "Feinzerlegung" this law was also followed fairly well by most of the components of Hβ and Hγ. Although a slight deviation from this law was observed in some of the components of Hδ, yet

this may be ascribed to experimental errors. With regard to $H\alpha$, comparing Stark's result obtained at 27500 volts per centimeter with that at 104000 volts per centimeter, the separation of its outermost parallel components was observed to increase proportionally with the strength of the electric field. Thus considered, it seems to be a general law that the displacement of each component of the Balmer lines of hydrogen increases proportionally with the strength of the electric field. In the following, this law was considered to be true of all the components of the Balmer lines of hydrogen.

In the tables, Table 1 and Table 2, the values of the displacements of the components of the Balmer lines observed by Stark at 104000 volts per centimeter are given. As the manner of decomposition of each of the Balmer lines is quite symmetrical with respect to their original undisplaced positions, only the result on the red-side-components is given in the tables.

The first regularity of the manner of decomposition which may easily be gathered from the tables is that the distance between any two successive components of either the parallel or the perpendicular component of a line is constant, so far as they belong to the same line. Some exceptions from this law are of course present, especially in the case of $H\gamma$. Next it is highly interesting to note that all the perpendicular components of $H\beta$ occupy exactly the same positions as those of the parallel ones.

Now in order to see whether there is a simple regularity or not among the electric components of the different Balmer lines, the writer calculated the displacements in wave number corresponding to those in wave length given by Stark as shown in Table 1, and Table 2.

As was stated before, the difference of displacements between any two neighbouring components of a line is constant. This is nearly true in the case of $H\alpha$, $H\beta$ and $H\delta$. And these constant differences in wave number of the neighbouring two components of these three lines are 6, 14 and 28 respectively, which are nearly integral multiples of 7. As regards the components of $H\gamma$, though with some exceptions, most of the differences of the two neighbouring components are nearly equal to 21 in wave number, which is equal to three times 7. Moreover the displacements in wave number of the components which are nearest to the original lines are nearly equal to some whole multiples of 7 in all the cases observed.

Observing these regularities and trying to express the displace-

ments in wave number of the components of the Balmer lines in a formula, the writer at last obtained the following two formulae.

$$\begin{cases} \Delta\nu_p = \frac{7}{10\cdot4}\{p(m-2)-4\}E = 0\cdot673\{p(m-2)-4\}E, \\ \Delta\nu_s = \frac{7}{10\cdot4}\{p(m-2)-6\}E = 0\cdot673\{p(m-2)-6\}E, \end{cases}$$

where $\Delta\nu_p$ and $\Delta\nu_s$ represent the displacement in wave number of a component in the parallel and in the perpendicular component respectively, $E$ is the strength of the electric field in $10^4$ volt per centimeter, and $p$ positive integers beginning from one and $m$ the term number of the series. The numerical values of $\Delta\lambda_p$ and of $\Delta\lambda_s$ at the field of $10\cdot4\times10^4$ volts per centimeter calculated by these formulae for different values of $p$, and for each value of $m$ corresponding to the first four lines of the Balmer series are given in Table 1 and Table 2. As may be seen from these tables the calculated values of $\Delta\lambda$ are in fair agreement with the observed values except for a few components of $H_\gamma$. This is also shown graphically in Fig. 1. Here the value of $\Delta\nu$ and the term number of the series $m$ are taken as the ordinate and abscissa respectively. Each straight line drawn in these figures represents the relation between the calculated value $\Delta\nu$ and the term number of the series $m$ corresponding to each value of $p$. The observed values of the displacements of the components expressed in wave number are represented by the points.

Recently the writer became aware that P. S. Epstein[1] had obtained a similar formula theoretically. But, so far as the writer knows, this is different in some points from those obtained by the writer.

Next, the Stark effect on the spectral lines of helium is somewhat more complicated than that of hydrogen. As is evident from the investigations made by Takamine and Yoshida[2], Nyquist[3] and Takamine and Kokubu[4], most of the spectral lines belonging to the diffuse series of helium have isolated components, in the electric field, on their immediate violet sides.

According to Takamine and Kokubu the line $\lambda$ 4472 has three such isolated components in the parallel and in the perpendicular

1 Epstein, Phys. Z.S., **17**, 148, (1916).
2 Takamine and Yoshida, Mem. Coll. Sci., Kyoto, **2**, 325, (1917).
3 Nyquist, Phys. Rev., **10**, 226, (1917).
4 Takamine and Kokubu, Mem. Coll. Sci., Kyoto, **3**, 81, (1918); and **3**, 275, (1919).

component respectively. And by exterpolating the displacements of these components, it was observed that all these six isolated components started from a common point in the zero field, so that they might be regarded as if they were originated from a rather hypothetical spectral line, so to speak, at $\lambda$ 4470.0 at the zero field. The term "isolated line" employed in the following description was used in such sense. The next member of the series, viz the line $\lambda$ 4026, had four and five isolated components in the parallel and in the perpendicular component respectively, of which the first three, both in the parallel and in the perpendicular component in the region of shorter wave length, started from an isolated spectral line at $\lambda$ 4025.4, and the remaining three isolated components originated also from an other isolated line at $\lambda$ 4025.9. In the case of the diffuse series of parhelium many such isolated components which might be regarded as due to the isolated lines at the zero field were also present, and the isolation of these isolated lines in the region of shorter wave length from the original lines became smaller as the term number of the series was increased. This was also the case in the isolated lines of helium. Moreover, the displacement in the electric field of the components of the original lines of the diffuse series of helium and parhelium was toward the region of longer wave length. The only one exception from this rule was the line $\lambda$ 5876 which was the first member of the diffuse series of helium. Next, the displacement of most of the isolated components of parhelium was toward the region of shorter wave length. This was also the case in helium, the only exception was that of the isolated perpendicular component originating from an isolated line $\lambda$ 4025.8 at the zero field, whose wave length was shorter by about 0·5 Å. U. than that of the original line at $\lambda$ 4026.3.

In the case of the line $\lambda$ 3819.9, which is the fourth member of the diffuse series of helium, four components were observed in the parallel and in the perpendicular components respectively. One half of these four components were in the region of shorter wave length, and the other half were in the region of longer wave length of the original line. All these components started from the original line at the zero field. and displaced proportionally with the intensity of the electric field. From the analogy of the manner of decomposition of the other lines in the electric field, the writer regarded the two p- and the two s-components which displaced toward the region of

shorter wave length from the original line as due to an isolated spectral line, whose isolation from the original line became very small as the term number of this line became larger. The remaining two p- and two s-components which displaced toward the region of longer wave length was considered to be the components of the original spectral line $\lambda$ 3819.9 in the electric field.

In the case of the line 4026.3, two isolated lines at $\lambda$ 4025.4 and $\lambda$ 4025.8 were imagined. It is, of course, not clear that the isolated line at $\lambda$ 3819.9 as was considered above corresponds to either of the two isolated lines of $\lambda$ 4026.3. But in the following the writer supposed, as a trial, that the components in the region of shorter wave length of $\lambda$ 3819.9 and all of those of the other lines of this series correspond to the components of the isolated line at $\lambda$ 4025.4 of the line $\lambda$ 4026.3.

In the case of the Balmer lines of hydrogen it was observed, as was described above, that the displacement of a component in the electric field increased proportionally with the intensity of the electric field. This was also the case in all the components of the first four lines of the diffuse series of helium.

Recently G. Liebert[1] investigated, using the method employed first by Stark, the effect of an electric field on the spectral lines of helium. His investigation was mainly concerned with the spectrum lines in the ultraviolet region. With regard to the lines of the diffuse series of helium, his results on the lines of the higher term number is especially important. He succeeded in observing many components of the lines at $\lambda$ 3705.15 and 3634.52. According to the same investigator, the separations of the outer components of these two lines were not proportional to the electric field

In the case of the line $\lambda$ 3705.15, the separation of the outer components increased nearly proportional to the insensity of the electric field; and a slight deviation of it from being proportional to the electric field might be ascribed to experimental errors, as the images of most of the outer components appeared broadened as was stated by Liebert. Next, with regard to the line $\lambda$ 3634.52, Liebert observed 6 p- and 6 s-components in the electric field of 17900 volts per centimeter, and 10 p- and 10 s- components in the field of 27500 volts per centimeter. As it appeared to the writer, that there was some

1 Liebert, Ann. d. Phys., 56, 589, (1918).

ambiguity about the correspondency between the outer components of the line in the two different electric fields, it was natural to consider that another component in one of the electric fields might correspond to the outer component in the other field. Taking the displacement of a component and the intensity of the electric field as the ordinate and the abscissa respectively, and plotting the values observed by Liebert at the field of 17900 and of 27500 volts per centimeter, it was found that each of the components of the line $\lambda$ 3634.52 at the field of 17900 volts per centimeter was nearly on a straight line passing throngh the origin and the point representing the displacement of a certain component in the field of 27500 volts per centimeter, as was shown in Fig. 3. This was also the case in all the components of the line 3705.15, as was shown in Fig. 2. Judging from these facts it seems natural to consider that the displacement of all the electric components of these two lines should increase proportionally with the intensity of the electric field as in the case of the other lines of the same series.

The electric components in the region of longer wave length of these two lines were regarded as due to the original spectrum lines of the diffuse series of helium, and those in the region of shorter wave length as due to the isolated spectrum lines as was considered in the case of the line $\lambda$ 3819.75 of the same series.

In the case of the diffuse series of parhelium, the isolated lines of this series were found by Liebert to form a new series of parhelium. With regard to the isolated lines of the diffuse series of helium, no such relation was as yet observed. But the writer supposes, at the present, that they are connected by a similar relation, and the same term number of the series as that of the diffuse series was affixed, for the sake of convenience, to the corresponding isolated line.

Trying to express the manner of decomposition of the lines of the diffuse series of helium and those of the series of the isolated lines separately by the formulae similar to those of the Balmer lines of hydrogen, the writer obtained the following formulae,

$$\begin{cases} \Delta\nu_p = 0{\cdot}673\,\{p(m-2)-2\}\,E, \\ \Delta\nu_s = 0{\cdot}673\,\{p(m-2)-6\}\,E \end{cases}$$

for the lines of the diffuse series of helium, and

$$\begin{cases} \Delta\nu_p = 0{\cdot}673\,\{p(m-2)-1\}\,E \\ \Delta\nu_s = 0{\cdot}673\,\{p(m-2)-3\}\,E \end{cases}$$

for the lines supposed to belong to a series of the isolated lines corresponding to the diffuse series of helium. In these formulae, $E$ represents the intensity of the electric field in $10^4$ volt per centimeter, $p$ positive integers beginning from I, $m$ the term number of the series, $\Delta\nu_p$ the displacement in wave number of a parallel component and $\Delta\nu_s$ represents the displacement of a perpendicular component.

The calculated values of $\Delta\lambda$ of the components of the lines belonging to the diffuse series of helium are tabulated in the tables from Table 3 to Table 7, and those values of $\Delta\lambda$ of the components of the

TABLE 3.

$\lambda$ 4472, $m=4$, diffuse series of helium.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. in Å.U. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. in Å.U. at $10\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. |
| 1 | 0·0 | 0·0 | 3 | 0·0 | 0·0 |
| 2 | 2·7 | 2·4 | 4 | 2·7 | 3·2 |
| 3 | 5·4 | 5·3 | 5 | 5·4 | 6·0 |
| 4 | 8·1 | 7·5 | 6 | 8·1 | 8·4 |
| 5 | 10.8 | | 7 | 10·8 | |

TABLE 4.

$\lambda$ 4026, $m=5$, diffuse series of helium.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ voltc/m. | $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. |
| 1 | 1·1 | — | 2 | 0·0 | — |
| 2 | 4·4 | — | 3 | 3·3 | — |
| 3 | 7·7 | 9·4 | 4 | 6·6 | — |
| 4 | 10·9 | 11·3 | 5 | 9·8 | 8·4 |
| 5 | 14·2 | 14·3 | 6 | 13·1 | 13·4 |
| 6 | 17·5 | — | 7 | 16·4 | 17·0 |
| | | | 8 | 19·7 | |

TABLE 5.

$\lambda$ 3819.9, $m=6$, diffuse series of helium.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $5\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $5\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $5\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $5\times10^4$ volt/cm. |
| 1 | 1·0 | — | 2 | 1·0 | — |
| 2 | 3·0 | 3·8 | 3 | 3·0 | 2·5 |
| 3 | 4·9 | — | 4 | 4·9 | — |
| 4 | 6·9 | — | 5 | 6·9 | — |
| 5 | 8·8 | 8·6 | 6 | 8·8 | 9·0 |
| 6 | 10·8 | | 7 | 10·8 | |

TABLE 6.

$\lambda$ 3705.15, $m=7$, diffuse series of helium.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. |
| 1 | 0·8 | — | 2 | 1·0 | — |
| 2 | 2·0 | — | 3 | 2·3 | — |
| 3 | 3·3 | 3·35 | 4 | 3·6 | 3·60 |
| 4 | 4·6 | — | 5 | 4·8 | — |
| 5 | 5·9 | — | 6 | 6·1 | — |
| 6 | 7·1 | 7·66 | 7 | 7·4 | — |
| 7 | 8·4 | — | 8 | 8·7 | 8·19 |

TABLE 7.

$\lambda$ 3634.52, $m=8$, diffuse series of helium.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. |
| 1 | 1·0 | 0·18 | 1 | 0·0 | 0.18 |
| 2 | 2·5 | 2·13 | 2 | 1·5 | 2.13 |
| 3 | 3·9 | — | 3 | 2·9 | — |
| 4 | 5·4 | 5·58 | 4 | 4·4 | — |
| 5 | 6·9 | — | 5 | 5·9 | 5·58 |
| 6 | 8·3 | — | 6 | 7·3 | — |
| 7 | 9·8 | 9·58 | 7 | 8·8 | 8·72 |

TABLE 8.

$\lambda$ 4470.0, $m=4$, series of isolated lines.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. |
| 1 | 1·3 | — | 2 | 1·3 | — |
| 2 | 4·0 | 4·2 | 3 | 4·0 | 3·9 |
| 3 | 6·7 | 7·7 | 4 | 6·7 | 6·4 |
| 4 | 9·4 | 10·1 | 5 | 9·4 | 9·8 |
| 5 | 12·1 | | 6 | 12·1 | |

TABLE 9.

$\lambda$ 4025.4, $m=5$, series of isolated lines.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $10\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $10\times10^4$ volt/cm. |
| 1 | 2·2 | — | 1 | 0·0 | — |
| 2 | 5·5 | — | 2 | 3·3 | — |
| 3 | 8·7 | — | 3 | 6·5 | — |
| 4 | 12·0 | 12·2 | 4 | 9·8 | 9·3 |
| 5 | 15·3 | 15·6 | 5 | 13·1 | 13·2 |
| 6 | 18·5 | — | 6 | 16·4 | 16·3 |
| 7 | 21·8 | 20·5 | 7 | 19·6 | |

TABLE 10.

$\lambda$ 3820, $m=6$, series of isolated lines.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $5\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $5\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $5\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $5\times10^4$ volt/cm. |
| 1 | 1·5 | — | 1 | 0·5 | — |
| 2 | 3·4 | 3·6 | 2 | 2·5 | 2·5 |
| 3 | 5·4 | — | 3 | 4·4 | — |
| 4 | 7·4 | — | 4 | 6·4 | — |
| 5 | 9·3 | 9·6 | 5 | 8·3 | 8·6 |
| 6 | 11·3 | — | 6 | 10·3 | — |

TABLE 11.

$\lambda$ 3705.2, $m=7$, series of isolated lines.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. |
| 1 | 1·0 | 1.09 | 1 | 0·5 | 0·01 |
| 2 | 2·3 | — | 2 | 1·8 | — |
| 3 | 3·6 | — | 3 | 3·1 | — |
| 4 | 4·8 | 5·40 | 4 | 4·3 | 4·42 |
| 5 | 6·1 | — | 5 | 5·6 | — |
| 6 | 7·4 | — | 6 | 6·9 | — |
| 7 | 8·6 | 9·14 | 7 | 8·1 | 8·09 |
| 8 | 9·9 | — | 8 | 9·4 | — |

TABLE 12.

$\lambda$ 3634.5, $m=8$, series of isolated lines.

| Parallel Component | | | Perpendicular Component | | |
|---|---|---|---|---|---|
| $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. | $p$ | $\Delta\lambda$ calc. at $2{\cdot}75\times10^4$ volt/cm. | $\Delta\lambda$ obs. at $2{\cdot}75\times10^4$ volt/cm. |
| 1 | 1·2 | — | 1 | 0·7 | — |
| 2 | 2·7 | 2·28 | 2 | 2·2 | 2·28 |
| 3 | 4·2 | — | 3 | 3·7 | — |
| 4 | 5·6 | 5·47 | 4 | 5·1 | 5·47 |
| 5 | 7·1 | 7·66 | 5 | 6·6 | — |
| 6 | 8·6 | — | 6 | 8·1 | 7·78 |
| 7 | 10·0 | — | 7 | 9·5 | — |
| 8 | 11·5 | 11·85 | 8 | 11·0 | — |
| 9 | 13·0 | — | 9 | 12·4 | 11·92 |
| 10 | 14·4 | 14·39 | 10 | 13·9 | 14·57 |
| 11 | 15·9 | — | 11 | 15·4 | — |
| 12 | 17·4 | — | 12 | 16·8 | — |
| 13 | 18·8 | 18·25 | 13 | 18·3 | 18·25 |
| 14 | 20·2 | — | 14 | 19·8 | — |

lines supposed to belong to a series of the isolated lines are given in tables from Table 8 to Table 12. And these results are also shown graphically in Fig. 4 and Fig. 5, which are drawn similarly as in the case of the Balmer lines of hydrogen. Here the values of $\Delta\nu$ at the field of $5\times10^4$ volt per centimeter are employed.

For the lines $\lambda$ 4472, $\lambda$ 4026 and $\lambda$ 3820, the values observed by

Takamine and Kokubu were utilised, and for the lines $\lambda$ 3705 and $\lambda$ 3634 those observed by Liebert were employed.

As is seen from the tables, the agreement between the observed and calculated values is fairly good in the case of most of the electric components of the 10 spectral lines before-mentioned. But there are, of course, some components which showed large deviations from the calculated values. Moreover many vacant spaces are left in the observed values. It was already stated that the line $\lambda$ 4026 had two isolated lines, and that the components belonging to the isolated line 4025.8 which was nearer to the original line $\lambda$ 4026 were disregarded; and the case might occur that some components which were really due to isolated lines corresponding to the isolated one of the 4026 at 4025·8 just mentioned were taken as those due to the others. All of those ambiguities above mentioned are to be made clear by future investigations, and a finer electric decomposition of the spectrum lines of helium like that of the Balmer lines obtained by Stark are highly desirable.

Lastly it is especially noteworthy that the constant 0·673 of the formulae for the lines of helium is entirely identical with that of the formulae for the Balmer series. This is also nearly equal to 0·660 for the Balmer lines obtained by Epstein theoretically.

In conclusion the writer's hearty thanks are due to Profs. T. Mizuno and M. Kimura for the interest they have taken in the research, and the writer also expresses his sincere thanks to Mr. M. Kiuchi of the University of Tokyo for his kind information of the results obtained by Stark on hydrogen.

Physical Laboratory,
Kyoto University,
September 31, 1919.

FIG. 1. (Balmer series)

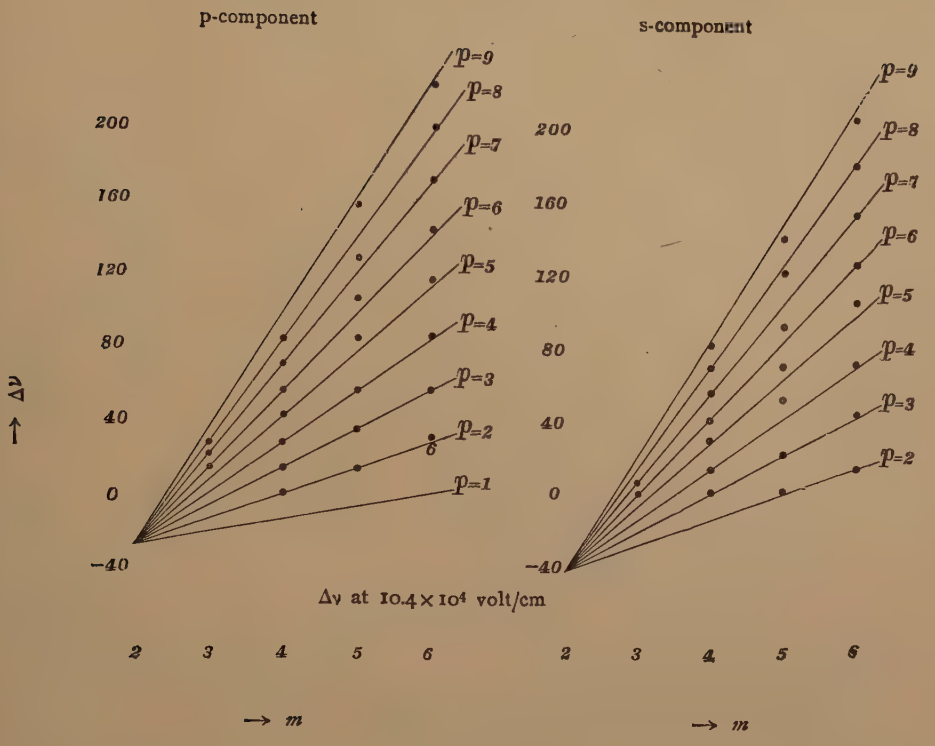
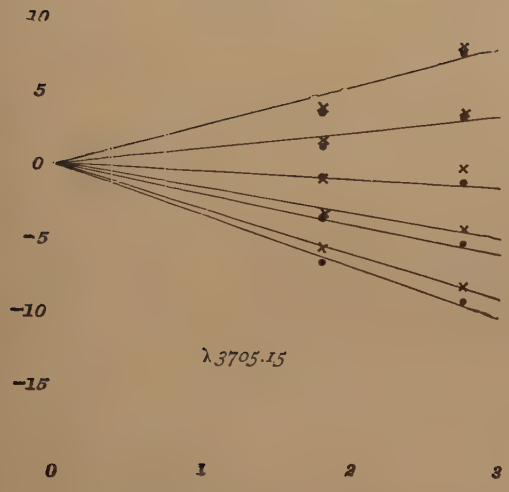
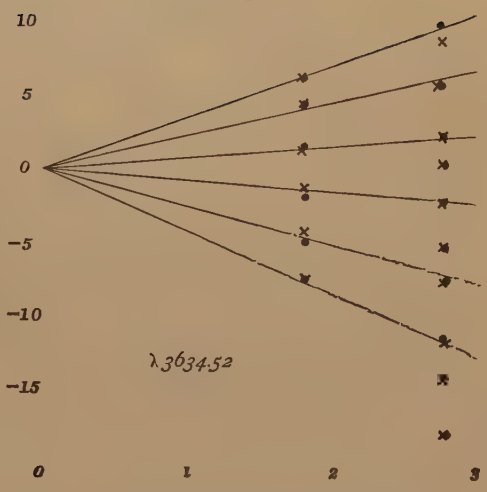


FIG. 2.




→ Electric field in $10^4$ volt/cm.

FIG. 3.




→ Electric field in $10^4$ volt/cm.

FIG. 4. (Diffuse series of helium)

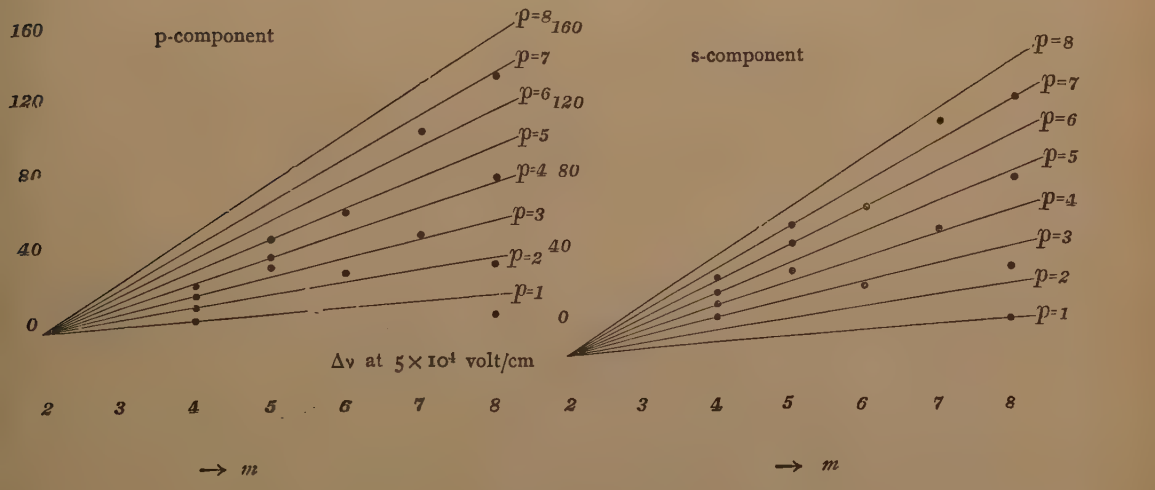
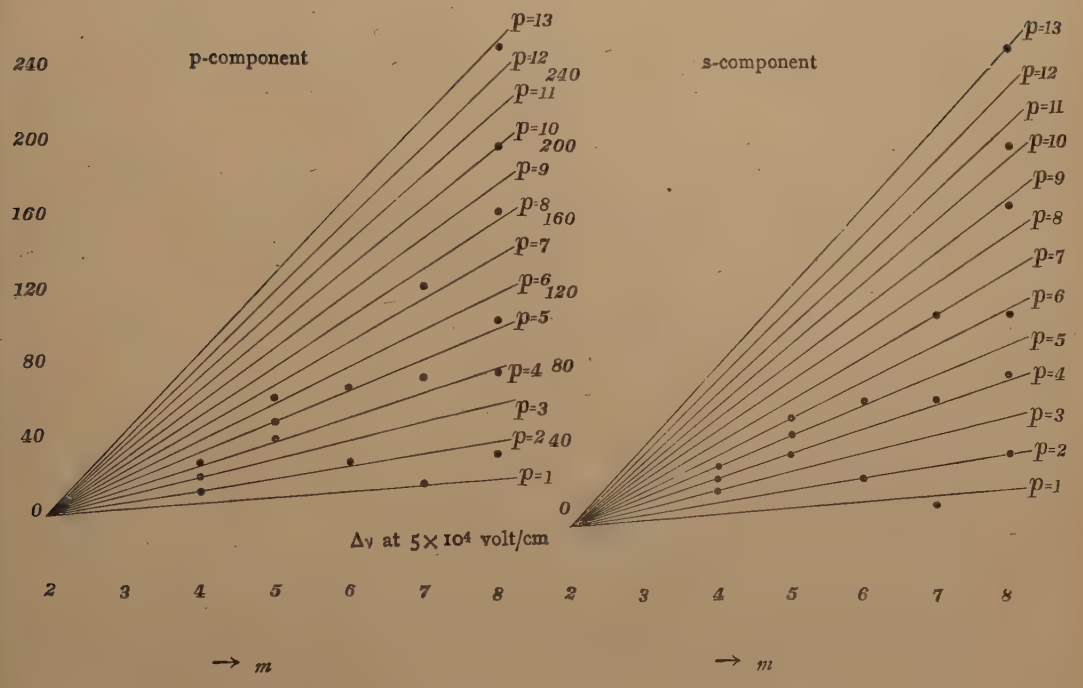


FIG. 5. (Series of isolated lines of helium)



# Constitution of the Salts of Aminoacetophenones

By

**Mitsuru Kuhara, Heikichi Saito and Akira Shimomura**

(Received Nov. 10, 1919)

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The authors have observed the interesting colour changes which the salts of o- and p-aminoacetophenone suffer under the influence of heat, solvents and some reagents, but not the salts of the meta compound[1]. In order to inquire after the causes of such phenomena, the absorption spectra of the different salts of the three isomeric aminoacetophenones have been studied under various conditions, and it has been found that the coloured salt of each of o- and p-aminoacetophenone in alcoholic solution shows a new absorption band in the visible region at the greater concentration than the broad band which is originally noticed in each.

A close analogy in the chemical conducts is found to exist between the salts of o-aminoacetophenone and those of the para isomer, but those of the meta isomer show a character wholly different from those of the other two isomers.

When colourless p-aminoacetophenone hydrochloride is heated at 100° for several hours, it acquires a deep yellow colour which gradually fades away on standing. The colourless and coloured salts both dissolve in alcohol under the exhibition of the same colouration, while their aqueous solution are almost colourless. The yellow colour of the alcoholic solution greatly weakens by passing an excess of dry

1 Kuhara and Ogawa first noticed a colour change of p-aminoacetophenone hydrochloride by heat,—unpublished work.

hydrochloric acid gas. Its sulphate likewise exhibits a pink colouration by heat.

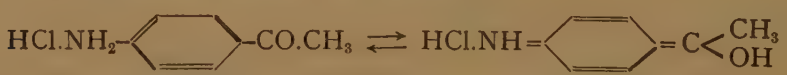
When o-aminoacetophenone hydrochloride which is also colourless is heated in the same way, a bright orange colouration takes place, which does not fade away even on a long standing. The coloured salt dissolves in water and in alcohol with an intense orange colour, while the freshly prepared aqueous or alcoholic solution of the colourless salt is almost colourless, but after a lapse of time the colours of alcoholic solutions of both salts assume the same tinge. The alcoholic solution of the orange salt also weakens in colour by adding an excess of hydrochloric acid, but the sulphate exhibits no colour change by heat unlike that of the para compound, in which a pink colouration actually occurs. The hydrochloride of its monomethyl derivative changes colour by heat, assuming deep orange red.

In the case of m-aminoacetophenone, its salt which is colourless undergoes no change of colour under the similar treatment, differently behaving from the ortho and para compounds.

It has also been observed that the hydrochloride of p-dimethylaminoacetophenone shows no change in colour by heat, and its alcoholic solution is colourless.

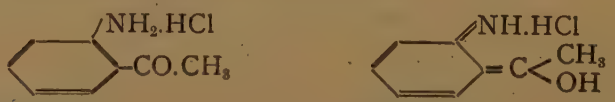
Inferring from the facts so far mentioned, it is highly probable that the colourless and yellow salts of p-aminoacetophenone are readily transformable to each other in alcoholic solutions, while in the ortho isomer the transformation is extremely slow. Now it is conceived that the coloured salts may take the quinoid form, while the colourless salts the benzoid, and as both colourless and coloured salts assume the same colouration in the solutions of the same concentration, the reversible isomeric change of keto-enol type may take place, probably forming an equilibrium mixture :

1. p-Aminoacetophenone hydrochloride.



Benzoid form. Colourless — Quinoid form. Yellow

2. o-Aminoacetophenone hydrochloride.



Benzoid form. Colourless — Quinoid form. Orange

m-Aminoacetophenone, unlike the ortho and para compounds can not undergo isomeric change to the quinoid form, inferring from the constitutional point of view.

Likewise, p-dimethylaminoacetophenone can not assume the quinoid form as it carries no movable hydrogen for rearrangement. In both cases, therefore, the isomeric change, viz. the alteration in constitution would evidently not take place. o-Monomethylaminoacetophenone hydrochloride may, however, take the quinoid form as it carries a movable hydrogen, and actually undergoes the colour change.

Baly and Marsden[1] have already carried out the spectrographic investigation with regard to the aromatic amino-aldehydes and -ketones, and give from the results of experiments the following conclusions:

"1. The amino-aldehydes and -ketones of the aromatic series in neutral alcoholic solution exhibit one broad absorption band.

"2. The addition of small quantities of alcoholic hydrogen chloride to the solution causes the development of a second absorption band, the first remaining unaltered, provided that insufficient acid has been added to produce the hydrochloride.

"3. It is not produced at all in aqueous solution.

"4. The phenomenon appears to be due to the amino-group; it is possible that the nitrogen atom is caused to functionate as a quinquevalent atom, so that the residual affinity is increased in the ratio of 5 to 3."

The experimental results by the authors almost coincide with those above-mentioned by Baly and Marsden, but the authors put forward somewhat different explanation, based upon the assumption that the coloured salts take the quinoid form as will be seen in the following statements:

1. Of the three isomeric aminoacetophenones the para shows the deepest absorption band, the ortho next and the meta compound the shallowest.

2. The coloured hydrochloride of each of the ortho and para compounds in alcoholic solution produces a new narrow absorption band toward the red at the greater concentration than the original broad band. The new bands of the two isomers resemble each other in their depth and position, and may be due to the quinoid form.

3. The aqueous solutions of the coloured salts do not exhibit

1 Baly and Marsden: J. Chem. Soc., 93, 2108, (1908).

the above phenomenon; this may be due to the change of the quinoid into the benzoid.

4. An excess of hydrochloric acid added to the alcoholic solutions of the coloured salts act so as to annual the characteristic new band in each case and makes general absorption much less; hence the action of hydrochloric acid seems to convert the quinoid into the benzoid form.

5. m-Aminoacetophenone and p-dimethylaminoacetophenone and their hydrochlorides do not manifest the second band; this may be due to the non-formation of the quinoid form.

## EXPERIMENTAL PART.

### 1. *p-Aminoacetophenone,* (p)$NH_2 \cdot C_6H_4 \cdot CO \cdot CH_3$

For the preparation of p-aminoacetophenone a method suggested by Klingel[1] was repeated by heating the equimolecular quantities of acetanilide, acetic anhydride and finely divided zinc chloride over an oil bath for 8 hours. The pasty mass thus formed was treated with hydrochloric acid in order to destroy all acetanilide, and after neutralised with caustic soda it was subjected to steam distillation to drive off all aniline. The residual brown oil, after repeated recrystallisation from hot water, gave colorless needles of p-aminoacetophenone melting at 105–106°. It is easily soluble in alcohol, ether or hot water; difficultly in cold water and almost insoluble in benzene or petroleum ether.

The substance was analysed with the following results:

I. 0·1092 grm. substance gave 0·2835 grm. $CO_2$ and 0·0670 grm $H_2O$.

II. 0·1230 grm. substance gave 0·3194 grm. $CO_2$ and 0·0755 grm. $H_2O$.

| | Calc. for $NH_2.C_6H_4CO.CH_3$ | Found I | Found II |
|---|---|---|---|
| C | 71·08 | 70·78 | 70·81 |
| H | 6·71 | 6·81 | 6·83 |

[1] Klingel: Ber. D. Chem. Ges., 18, 2688, (1885).

p-Aminoacetophenone hydrochloride was prepared by passing dry hydrochloric acid gas through an ethereal solution of the base. The hydrochloride consisting of colorless needle shaped crystals thus obtained is easily soluble in water or alcohol, and insoluble in ether, benzene, chloroform or petroleum benzine. The colorless salt changes deep yellow on heating at 100° for several hours, but on standing it gradually fades assuming a pale yellow color. Both colorless and yellow salts dissolve in water, giving almost colorless solutions, but in alcohol with a distinct yellow color. It is also observed that the yellow color of the alcoholic solution much weakens by an excess of hydrogen chloride and becomes colorless at last.

The analysis of the colorless and yellow salts gave the following values of chlorine:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| I. | 0·3000 | grm. | colorless | salt | gave | 0·2518 | grm. | AgCl. |
| II. | 0·2000 | ,, | ,, | ,, | ,, | 0·1638 | ,, | ,, |
| III. | 0·2600 | ,, | yellow | salt | ,, | 0·2237 | ,, | ,, |
| IV. | 0·3051 | ,, | ,, | ,, | ,, | 0·2492 | ,, | ,, |

| Calc. for HCl. $NH_2.C_6H_4.CO.CH_3$ or HCl. $NH:C_6H_4:COH.CH_3$ | | Found | | | |
|---|---|---|---|---|---|
| | | Colorless salt | | Yellow salt | |
| Cl | 20·67 | I. | 20·73 | III. | 21·27 |
| | | II. | 20·26 | IV. | 20·21 |

It is almost evident that p-aminoacetophenone hydrochloride exists in two desmotropic forms, and the colored alcoholic solution would be an equilibrium mixture of the two.

By measuring the molecular weights of the differently colored salts, it is certain that such a change as polymerisation has not taken place.

p-Aminoacetophenone sulphate was prepared by adding a drop of conc. sulphuric acid into an ethereal solution of the base. It is soluble in water or alcohol, but more difficultly than the hydrochloride, and insoluble in ether, chloroform, benzene or petroleum ether. The sulphate undergoes the similar change in color, becoming pink on heating at 100° for several hours, and these colorless and pink sulphates bear the same relation to the colorless and yellow hydrochlorides.

The pink salt was analysed with the following results:

0.3650 grm. pink salt gave 0.2331 grm. $BaSO_4$.

| Calc. for $C_{16}H_{20}N_2O_2.SO_4$ | | Found |
|---|---|---|
| $SO_4$ | 26·08 | 26·28 |

## 2. *p-Dimethylaminoacetophenone*, $(p)(CH_3)_2N.C_6H_4.CO.CH_3$

p-Dimethylaminoacetophenone was prepared by heating 1 part p-aminoacetophenone and 2 parts methyl iodide in methyl alcohol at 180–200° for 6 hours in a sealed tube. Moreover, following the method of the preparation of m-dimethylaminoacetophenone[1], p-aminoacetophenone, methyl iodide, soda and water were heated in a flask provided with a reflux condenser for several hours, and the same dimethyl compound was obtained.

It consists of platy colorless crystals melting at 105°, and easily soluble in alcohol, ether or hot water, but insoluble in cold water or petroleum ether.

I. 0·1507 grm. substance gave 0·3981 grm. $CO_2$ and 0·1147 grm. $H_2O$.

II. 0·1333 grm. substance gave 0·3570 grm. $CO_2$ and 0·1123 grm. $H_2O$.

| Calc. for $(CH_3)_2N.C_6H_4.CO.CH_3$ | | Found I | Found II |
|---|---|---|---|
| C | 73·58 | 72·07 | 72·99 |
| H | 8·03 | 8·45 | 8·71 |

p-Dimethylaminoacetophenone hydrochloride undergoes no change in color by heat.

I. 0·3020 grm. substance gave 0·2188 grm. AgCl.

II. 0·1314 „ „ „ 0·0895 „ „

| Calc. for $C_{10}H_{14}NOCl$ | | Found I | Found II |
|---|---|---|---|
| Cl | 17·76 | 17·92 | 17·28 |

It melts at 147–148° with decomposition.

p-Dimethylaminoacetophenone picrate was prepared by mixing the

[1] Rupe, Braun and Zembruski: Ber. D. Chem. Ges., **34**, 3524 (1901).

alcoholic solutions of the two components. It consists of yellow crystals melting at 124° with decomposition.

0·1200 grm. substance gave
0·2108 grm. $CO_2$ and 0·0455 grm. $H_2O$.

| | Calc. for $CH_3CO.C_6H_4.N(CH_3)_2.C_6H_2.(NO_2)_3.OH$ | Found |
|---|---|---|
| C | 47·36 | 47·91 |
| H | 4·24 | 4·33 |

## 3. *Absorption Spectra of p-Aminoacetophenone and its Hydrochloride*[1]

The following five cases have been spectrographically studied:

(1) p-Aminoacetophenone in alcohol. (Fig. 1)
(2) p-Aminoacetophenone hydrochloride in alcohol. (Fig. 1)
(3) „ „ + excess of HCl in alcohol. (Fig. 1)
(4) „ „ in water. (Fig. 2)
(5) „ „ + excess of HCl in water. (Fig. 2)

They all show respectively a broad band at the vicinity of 3100. It is quite characteristic that the yellow alcoholic solution of p-aminoacetophenone hydrochloride develops a new small band at 2460 when the solution is more concentrated, the first broad band remaining unaltered (2), while it disappears in an excess of hydrogen chloride (3). On the other hand, the colorless or yellow salt in aqueous solution as well as in hydrochloric acid exhibits only one broad band (4) (5). It has been noted that the excess of hydrogen chloride makes the band shallower and less absorptive (3) (5).

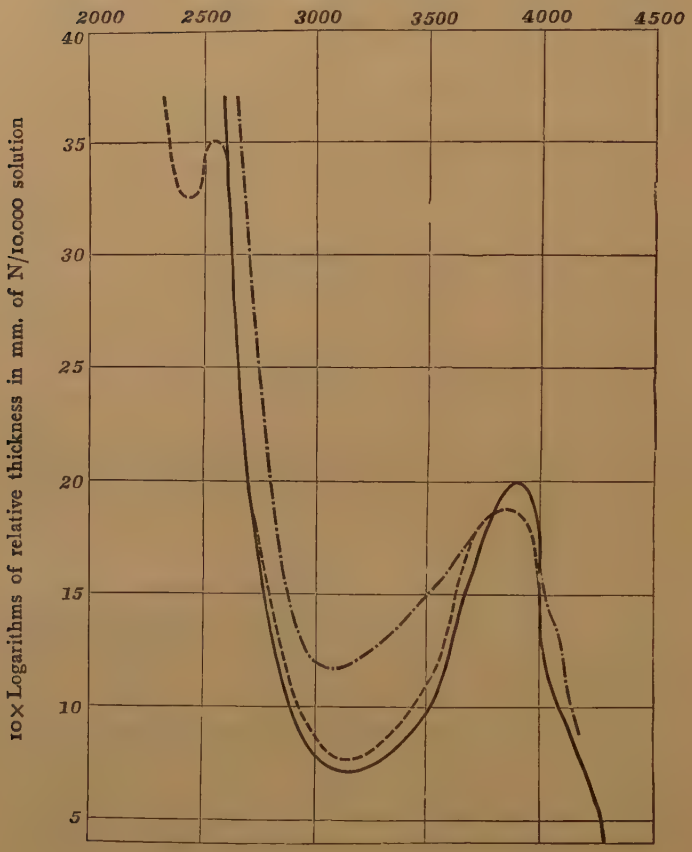
## 4. *Absorption Spectra of p-Dimethylaminoacetophenone and its Hydrochloride*

p-Dimethylaminoacetophenone and its hydrochloride, in alcoholic solution, exhibit only one broad band at 3000 in each case (Fig. 3). A new band is not developed when hydrochloride is dissolved in alcohol. It has been noted that these absorptions are slightly shifted toward the red as compared to those of the primary amine and its salt.

1 Baly and Marsden: J. Chem. Soc., 93, 2108 (1908).

FIG. 1.

Oscillation frequencies




(1) p-Aminoacetophenone in alcohol.
(2) p-Aminoacetophenone hydrochloride in alcohol.
(3) „ „ + HCl in alcohol.

## 5. *o-Aminoacetophenone*,

(o)$NH_2.C_6H_4.CO.CH_3$

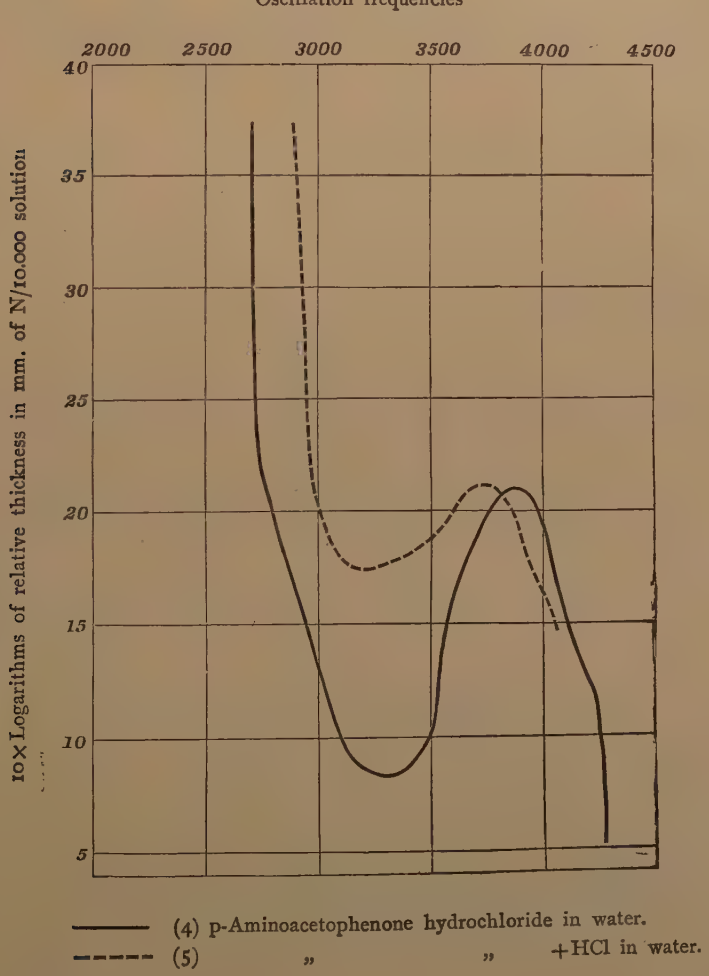
o-Aminoacetophenone has been prepared according to Camps' method[1] by reducing o-nitroacetophenone with tin and hydrochloric acid. It is a pale yellow oil with a peculiar smell, which slowly

1 Camps: Ar. Ph., **240**, 6 (1902).

turns reddish when exposed to light and air. It is soluble in alcohol, ether, benzene or petroleum benzine, but almost insoluble in water.

o-Aminoacetophenone hydrochloride[1] was prepared by passing dry hydrogen chloride through an ethereal solution of the base, cooled with ice cold water. Colorless fine needles soon appeared which were quickly filtered and dried in vacuum. The salt is easily soluble in water, giving an almost colorless solution, soluble in alcohol with pale yellow color, but insoluble in ether, benzene, chloroform or petroleum benzine.

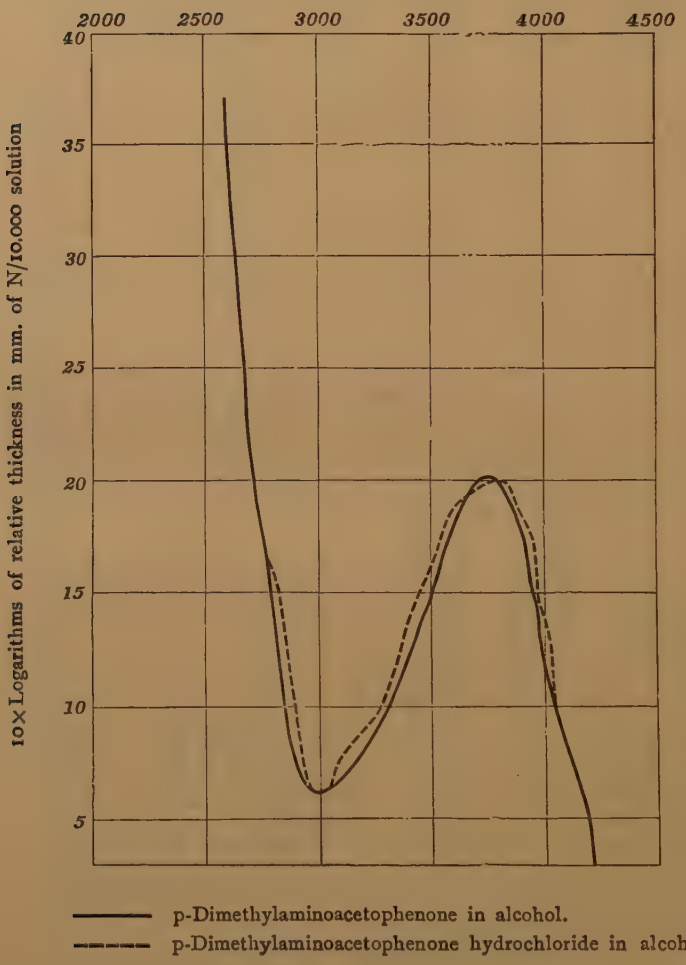
FIG. 2.




1 Baeyer and Bloem: Ber. D. chem. Ges., **15**, 2154 (1882).

FIG. 3.

Oscillation frequencies




When the colorless hydrochloride was heated at 100°, it slowly assumed a yellowish orange color, and after 4 hours it became bright orange, which did not seem to fade on standing. The colored salt is soluble in water or alcohol, giving orange colored solutions, the color being more intense in the latter one. An excess of hydrogen chloride weakens the color of aqueous as well as alcoholic solution of the colored salt.

I. 0·2037 grm. colorless salt gave 0·1681 grm. AgCl.
II. 0·2049 „ „ „ „ 0·1701 „ „
III. 0·1534 „ orange salt „ 0·1301 „ „
IV. 0·1320 „ „ „ „ 0·1081 „ „

| Calc. for $HCl.NH_2.C_6H_4.CO.CH_3$ | | Found | | | |
|---|---|---|---|---|---|
| | | Colorless salt | | Orange salt | |
| Cl | 20·67 | I. | 20·36 | III. | 20·98 |
| | | II. | 20·54 | IV. | 20·26 |

o-Aminoacetophenone sulphate[1] consists of colorless crystals, soluble in water, difficultly in alcohol, and insoluble in ether, benzene, chloroform or petroleum benzine. It does not show any change in color by the heat treatment.

## 6. *m-Aminoacetophenone*, $(m)NH_2.C_6H_4.CO.CH_3$

Hitherto several methods[2] have been proposed for the reduction of m-nitroacetophenone, but we adopted Camps' method[3] which affords easy manupilation and a satisfactory yield.

m-Aminoacetophenone thus obtained consists of pale yellow, odorless, shiny scales, melting at 95–96°. It is almost insoluble in cold water but fairly in hot water; soluble in alcohol or ether, difficultly in benzene, but insoluble in petroleum benzine.

m-Aminoacetophenone hydrochloride[4] was prepared in the same way as the ortho compound. It does not show any perceptible change in color by heating at 100° for 4 hours. It has similar solubilities in various solvents as the ortho compound.

I. 0·2184 grm. substance gave 0·1831 grm. AgCl.
II. 0·1932 „ „ „ 0·1621 „ „
III. 0·1535 „ substance (after heating) gave 0·1281 grm. AgCl.

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1 Baeyer and Bloem: loc. cit.
Gevekoht: Lieb. Ann., **221**, 326 (1883).
2 Engler: Ber. D. chem. Ges., **11**, 932 (1878).
Konstanecki and Tambor: Ber. D. chem. Ges., **34**, 1691 (1901).
Rupe, Braun and Zembruski: Ber. D. chem. Ges., **34**, 3522 (1901).
3 Camps: loc. cit.
Hunnius: Ber. D. chem. Ges., **10**, 2009 (1877).

| Calc. for $HCl.NH_2.C_6H_4.CO.CH_3$ | | Found | | | |
|---|---|---|---|---|---|
| Cl | 20·67 | I. | 20·74 | III. | 20·64 |
| | | II. | 20·76 | | |

m-Aminoacetophenone sulphate also undergoes no change in color by heat.

## 7. *Absorption Spectra of o-Aminoacetophenone and its Hydrochloride*[1]

The following six cases have been spectrographically examined:

(1) o-Aminoacetophenone in alcohol. (Fig. 4)
(2) o-Aminoacetophenone hydrochloride (colorless) in alcohol. (Fig. 4)
(3) „ „ (orange) in alcohol. (Fig. 4)
(4) „ „ (orange) + excess of HCl (7.7 N) in alcohol. (Fig. 4)
(5) „ „ (colorless) in water. (Fig. 5)
(6) „ „ (orange) in water. (Fig. 5)

They all show respectively a broad band at the vicinity of 2700. The absorption curve of the free amine (1) coincides with that of the colorless hydrochloride (2). The orange salt, in alcohol, likewise develops a new small band in the visible region (2180) at a greater concentration (3), the main band remaining unaltered as in the case of the para compound. On the other hand, the same orange salt in alcoholic hydrochloric acid (7.7 N acidity) shows much less general absorption (4), losing the second band characteristic to the colored salt. The colorless and orange salts exhibit almost identical curves in aqueous solution, having only one broad band at 2850 in each case (5) (6).

## 8. *Absorption Spectra of m-Aminoacetophenone and its Hydrochloride*

The following four cases have been examined:

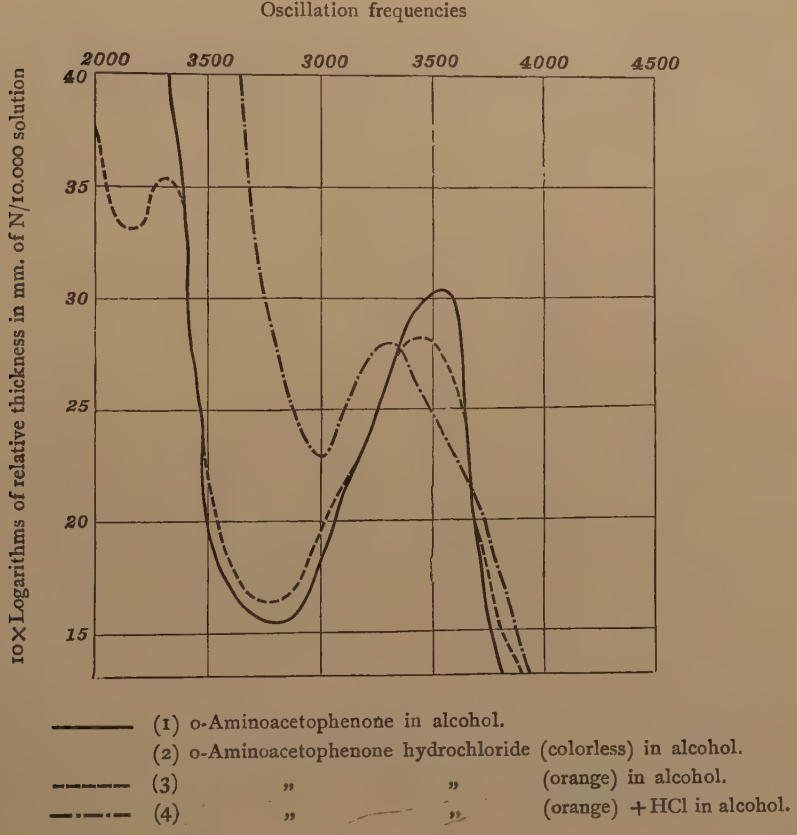
(1) m-Aminoacetophenone in alcohol. (Fig. 6)
(2) m-Aminoacetophenone hydrochloride in alcohol. (Fig. 6)
(3) „ „ (after heated at 100° for 4 hours) in alcohol. (Fig. 6)
(4) „ „ in water. (Fig. 6)

[1] Baly and Marsden: loc. cit.

The general form of their absorption curves resembles those of the ortho and the para compounds, but it has been noted that the band is markedly shallower in each case.

The hydrochloride, after heated at 100° for 4 hours, in alcoholic solution (3) gives almost identical curve with that of the original salt (2), showing that no change has taken place in its constitution.

FIG. 4.




## 9. *Alkyl Derivatives of o- and p-Aminoacetophenone*

Intending to prepare the dimethyl derivative of o-aminoacetophenone, several experiments have been carried out, but all ended in negative results. By a prolong heating of o-aminoacetophenone, methyl iodide and potassium hydroxide in methyl alcohol, o-mono-

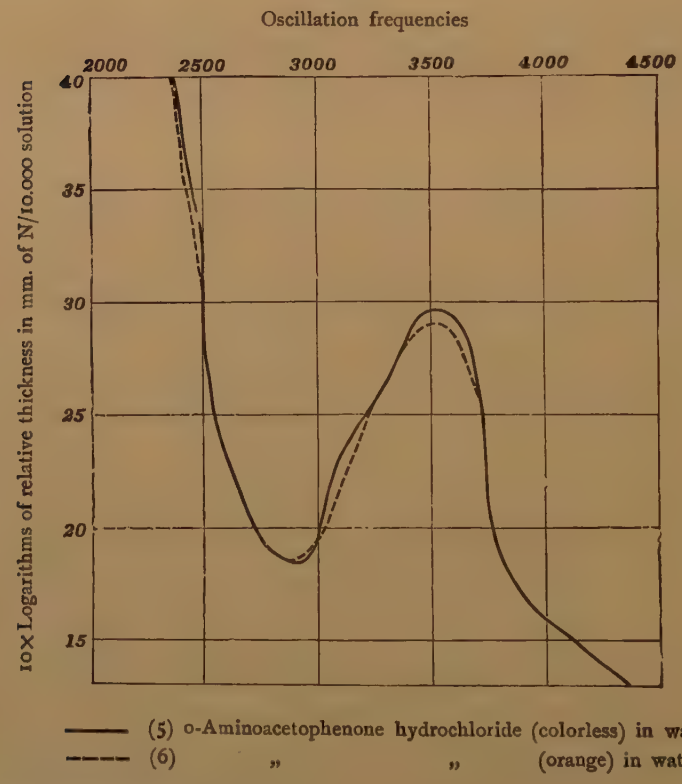
methylaminoacetophenone was prepared, whose hydrochloride seems to take the quinoid form by rearrangement as it assumes a deep orange color by heat.

I. 0·1037 grm. original hydrochloride gave 0·0802 grm. AgCl.
II. 0·1080 „ heated „ „ 0·0816 „ „

| Calc. for $HCl.(CH_3)NH.C_6H_4.CO.CH_3$ | | Found | |
|---|---|---|---|
| Cl | 19·11 | I. | 19·13 |
| | | II. | 18·79 |

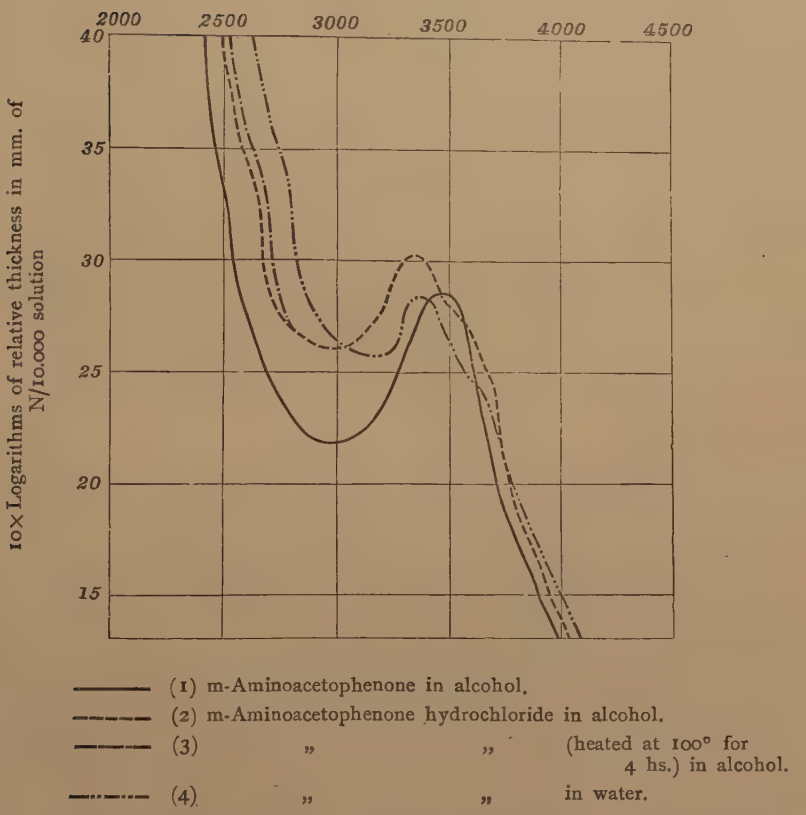
m-Dimethylaminoacetophenone was easily prepared according to Rupe, etc.[1] from m-aminoacetophenone, methyl iodide and soda in an aqueous solution. When the reaction mass was cooled, there separated out copious light brown leafy crystals, which after treatment with

FIG. 5.




1 Rupe, Braun and Zembruski: loc. cit.

FIG. 6.




animal charcoal and recrystallisation from hot water, gave colorless shiny platy crystals of trimethyl-m-acetophenyl ammonium iodide $(m)N(CH_3)_3I.C_6H_4.CO.CH_3$, which melts at 195° with decomposition into m-dimethylaminoacetophenone, giving off methyl iodide. m-Dimethylaminoacetophenone hydrochloride does not undergo a change in color by heat.

0.1350 grm. substance gave 0.0961 grm. AgCl.

| Calc. for $HCl.(CH_3)_2N.C_6H_4.CO.CH_3$ | | Found |
|---|---|---|
| Cl | 17.76 | 17.62 |

# On Organic Compounds of Arsenic. I

## Reaction between the Grignard Reagent and Arsenious Chloride

By

**Kaoru Matsumiya**

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The action of the halides of metals and metalloids on the Grignard reagent has been widely utilized as the general reaction for the synthesis of the organo-metallic, and -metalloid, compounds. This reaction was discovered by P. Pfeiffer[1], and in the same year, V. Auger and M. Billy[2], W. I. Pope and S. J. Peachey[3] published the results of their researches on the same subject. Pfeiffer and Pope further continued their investigations in the same direction[4], and Pfeiffer[5] finally proposed the following general equation for the reaction.

$$MX_n + mRMgX = MR_mX_{n-m} + mMgX_2$$

Taking great interest in this reaction, the author studied it in connection with the preparation of the organic derivatives of arsenic. In almost all cases recorded in this field, the halogen atoms combined with arsenic were completely replaced by alkyl or aryl radicals, corresponding to the case when $m=n$ in the above equation. The

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1 P. Pfeiffer and K. Schnurmann, Ber. D. Chem. Ges., **37**, 319, (1904); P. Pfeiffer and P. Truskier, Ber. D. Chem. Ges., **37**, 1125, (1904); P. Pfeiffer, I. Heller and H. Pietsch, Ber. D. Chem. Ges., **37**, 4620, (1904).

2 V. Auger and M. Billy, C. R., **139**, 597, (1904).

3 W. I. Pope and S. J. Peachey, Proc. Chem. Soc., **19**, 290, (1904).

4 P. Pfeiffer and R. Prade, Ber. D. Chem. Ges., **44**, 1273, (1911); S. Möller and P. Pfeiffer, J. Chem. Soc., **112**, 1, 122, (1917); W. J. Pope and S. J. Peachey, Proc. Chem. Soc., **23**, 86, (1907); J. Chem. Soc., **95**, 571, (1909).

5 P. Pfeiffer and K. Schnurmann, loc. cit.

author, therefore, attempted to restrain the reaction so as to replace any desired number of the halogen atoms attached to arsenic by organic radicals. For this purpose several experiments have been carried out, and in the present paper the author has to communicate the results of his researches on the aryl compounds of arsenic.

According to Pfeiffer's method, arsenious halide was added to the Grignard reagent in the proportion of one molecule of aryl magnesium halide for each halogen atom of arsenious halide. The main product of the reaction was always tertiary arsine compound; primary and secondary compounds were obtained only as by-products. The reaction is represented thus,

$$3RMgX + AsX_3 = R_3As + 3MgX_2$$

The reaction between arsenious halide and the Grignard reagent, however, may be presumed to take place in the following three stages.

$$AsX_3 + RMgX = RAsX_2 + MgX_2 \qquad \text{(i)}$$

$$RAsX_2 + RMgX = R_2AsX + MgX_2 \qquad \text{(ii)}$$

$$R_2AsX + RMgX = R_3As + MgX_2 \qquad \text{(iii)}$$

If this be the case, the proportion of the two compounds in action may be expected to have some effect on the reactions. In order to ascertain this point experimentally, the Grignard reagent prepared from $\alpha$-bromonaphthalene and magnesium, was treated with arsenious chloride in a molecular proportion. Contrary to expectation, tri-$\alpha$-naphthylarsine was obtained with a good yield. Phenylmagnesium bromide was also found to react with arsenious chloride in an exactly analogous way and produced triphenylarsine as the main product.

The experiments, above stated were conducted, as usual, by adding an ethereal solution of arsenious chloride to the Grignard reagent, so that the action accompanying each addition of the former evidently took place always in presence of an excess of the latter.

Now it is necessary to study the effect produced when an excess of an ethereal solution of arsenious chloride acted on aryl magnesium bromide. For this purpose, the Grignard reagent was allowed to drop upon an ethereal solution of arsenious chloride, the proportion having been taken as in equation I. In this connection, the work of Auger and Billy[1] should be mentioned who studied the action of methyl-

1 V. Auger and M. Billy, loc. cit.

magnesium bromide on phosphorous chloride, ethylmagnesium bromide on arsenious chloride and on antimonious chloride in this way, and obtained three kinds of methylphosphine and ethylarsine compounds, and a monoethylstibine compound.

The reaction thus brought about was vigorous and a quantity of precipitate, which was found to belong to the type $R_2AsX$, was produced. Although the expected primary arsine compound was not obtained, the effect of the different mode of application of the Grignard reagent was thus confirmed. The author proposes this way of working as the best synthetical method for secondary aryl arsine compounds. In the experiments, the following results were obtained :—

With the phenyl compound, in the usual process, the chief product was triphenylarsine, while in the author's process it was diphenylarsenious chloride. With the naphthyl compound, tri-$\alpha$-naphthylarsine was mainly produced in the usual process while in the author's process the chief product was di-$\alpha$-naphthylarsenious chloride in a yield of about 60 percent of the calculated amount.

Tri-$\alpha$-naphthylarsine was prepared with Grignard reagent in a yield of about 70 percent of the calculated amount, while it was obtained by sodium method in a yield of 20 percent.

## EXPERIMENTAL PART

### 1. *Action of Arsenious Chloride upon Phenylmagnesium Bromide*

32·5 grm. of bromobenzene were treated with 5 grm. of magnesium and a piece of iodine in dry ether. To the ethereal solution of phenylmagnesium bromide thus obtained, 37·5 grm. of arsenious chloride dissolved in dry ether were cautiously added and a white precipitate was produced. Then it was boiled for about one hour so as to complete the reaction. After it was well cooled, the ethereal solution was treated with water which completely composed the precipitate. A small quantity of a white substance which remained insoluble in ether and water, was proved, by its chemical reaction to be arsenious oxide. The ethereal solution was filtered and evaporated. A colourless crystal and a small quantity of yellowish-coloured oil were obtained. To isolate the tertiary arsine completely, the whole substance was dissolved in ether again and treated with an ethereal

solution of mercuric chloride[1], until the white precipitate ceased to be produced. Then the double salt was dissolved in boiling absolute alcohol and then alcoholic potash was added in an excess, whereby mercuric oxide instantly formed as a reddish brown precipitate. The precipitate was filtered off and the filtrate was saturated with carbon dioxide, filtered again and the solution concentrated and set aside. Colorless crystals were formed which, on recrystallising from alcohol, melted at 59–60°. The yield was 10·5 grm. The arsenic was estimated by Ewins' method[2].

0·1901 grm. substance required 24·9 c. c. of N/20 iodine solution.

| | Calc. for $(C_6H_5)_3As$ | Found |
|---|---|---|
| As | 24·45 | 24·56 |

## 2. *Action of Phenylmagnesium Bromide upon Arsenious Chloride*

The ethereal solution of phenylmagnesium bromide, prepared from 32·5 grm. of bromobenzene and 5 grm. of magnesium, was added to 37·5 grm. of arsenious chloride in dry ether. A brisk reaction took place on each addition, causing a white precipitate. After boiling for an hour, it was cooled well and then treated with water. The precipitate was decomposed so energetically that the solution strongly boiled. When the reaction subsided, the whole solution became quite clear, only a small quantity of arsenious oxide remaining at the bottom. On evaporating off the ether, only a yellow coloured oil was obtained. The whole substance was dissolved in ether again and treated with an ethereal solution of mercuric chloride to remove the triphenylarsine. A small quantity of a white precipitate formed was filtered off and the ethereal solution was repeatedly shaken with water containing hydrochloric acid so as to remove the mercuric chloride. The washing was repeated until the aqueous layer no longer became coloured by the hydrogen sulphide. The ethereal solution was dried with calcium chloride and then distilled. The distillate between 300–350° was a yellow oil, which, from its properties, was proved to be diphenylarsenious chloride. The yield was 12 grm.

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1 A. Michaelis, Ann., **321**, 141, (1902).

2 A. J. Ewins, J. Chem. Soc., **109**, 1355, (1916).

As a portion having a constant boiling-point was hardly obtainable, the whole substance was transformed to diphenylarsinic acid by the usual method. That is, the oil was dissolved in ether and the ethereal solution was saturated with chlorine, when a slightly yellow-coloured precipitate was formed. The whole substance was decomposed with water and the aqueous solution was evaporated to dryness. The remaining solid was recrystallised from ether. Colourless needles thus produced melted at 173–174°. Its analysis gave the following value for arsenic.

0·2079 grm. substance required 31·7 c.c. of N/20 iodine solution.

| | Calc. for $(C_6H_5)_2AsO.OH$ | Found |
|---|---|---|
| As | 28·63 | 28·59 |

### 3. *Preparation of Tri-α-naphthylarsine*

62·5 grm. of α-bromonaphthalene, 7·2 grm. of magnesium and a piece of iodine were added to an ample quantity of dry ether and boiled on a water bath under a reflux condenser until the magnesium was completely dissolved. 18·2 grm. of arsenious chloride dissolved in dry ether, were little by little poured upon the ethereal solution of α-naphthylmagnesium bromide. An energetic reaction took place and a white precipitate was formed which was at first redissolved by shaking but subsequently became permanent. After distilling off the ether, the residue was treated with water and the insoluble matter was collected and dried. This product was extracted with hot benzene, concentrated somewhat and treated with alcohol, when a slightly yellow-coloured crystalline deposit was obtained. On recrystallising from a mixture of benzene and alcohol, colourless crystals melting at 248° were finally obtained. The yield was 33 grm. The analytical results were as follows:

0·1305 grm. of the sample gave 0·3759 grm. $CO_2$ and 0·0567 grm. $H_2O$

0·1060 grm. substance required 9 c.c. of N/20 iodine solution.

| | Calc. for $(C_{10}H_7)_3As$ | Found |
|---|---|---|
| C | 78·95 | 78·56 |
| H | 4·61 | 4·83 |
| As | 16·44 | 15·85 |

### 4. *Action of Arsenious Chloride upon α-Naphthylmagnesium Bromide*

36·4 grm. of arsenious chloride in dry ether were added to an ethereal solution of α-naphthylmagnesium bromide, prepared with 41·4 grm. of α-bromonaphthalene and 5 grm. of magnesium in dry ether. After boiling for an hour, the ether was distilled off and the residue treated as in the former case. Colourless crystals were obtained which melted at 248°. The yield was 20 grm. The substance was analysed and the value of arsenic was found as follows:

0·0722 grm. substance required 6·2 c.c. of N/20 iodine solution.

| | Calc. for $(C_{10}H_7)_3As$ | Found |
|---|---|---|
| As | 16·44 | 16·10 |

### 5. *Action of α-Naphthylmagnesium Bromide upon Arsenious Chloride*

A solution of α-naphthylmagnesium bromide, prepared with 41·4 grm. of α-bromonaphthalene and 5 grm. of magnesium in dry ether, was added drop by drop to 36·4 grm. of arsenious chloride dissolved in dry ether, with constant cooling and shaking. Each drop caused a hissing sound and produced a precipitate. To complete the reaction, the mixture was boiled for an hour, cooled well and water was added cautiously. A brisk reaction took place and the precipitate was almost dissolved. The ethereal solution was washed with water and filtered. On distilling off the ether, a yellow mass was obtained, which was dissolved in hot alcohol-benzene and decolourised with animal charcoal. Fine crystals thus obtained were slightly yellow-coloured and melted at 116–117°. The yield was 21 grm. It was recrystallised three times from alcohol-benzene and analysed. The results were as follows:

0·1208 grm. of the substance gave 0·2921 grm. $CO_2$ and 0·0448 grm. $H_2O$.

0·0740 grm. substance required 7·8 c.c. of N/20 iodine solution.

Chlorine was estimated by Dean and Wilcox's method[1].

1 W. M. Dean and B. B. Wilcox, Amer. Chem. J., **1**, 7, (1906).

0·1469 grm. substance required 0·0659 grm. silver nitrate.

| | Calc. for $(C_{10}H_7)_2AsCl$ | Found |
|---|---|---|
| C | 65·84 | 65·95 |
| H | 3·84 | 4·12 |
| As | 20·58 | 19·76 |
| Cl | 9·74 | 9·39 |

Di-α-naphthylarsenious chloride is slightly soluble in alcohol, sparingly soluble in hot alcohol and ether, easily soluble in benzene, carbon bisulphide and carbon tetrachloride, more readily so in hot benzene and chloroform.

# On the Solutions of Partial Differential Equations of the First Order at the Singular Points. III.

By

**Toshizô Matsumoto.**

(Received March 18, 1920)

## INTRODUCTION.

The problem of the partial differential equations is a never-ending one among mathematicians from ages ago. After the researches of Cauchy[1], Jacobi and Riemann[2]; during 1870, much remarkable progress was made: Mayer[3] found the method of the solution of Jacobi's system in 1872. The demonstration of Kowalewski[4] appeared in 1875. The first fundamental theorem of Lie's group was written in 1876. Among the many works of Darboux[5], the remarkable memoir on the singular solutions of partial differential equations of the first order was presented to the Academy of Paris in 1877. Poincaré, as we have said in the preceding volume of these memoirs[6], presented his thesis concerning the solutions of partial differential equations of the first order at the singular points in 1879. Cauchy established the existence theorem by the method of the calculations of limits. But in

1 Existence theorem; C. R. (1842–43).
2 Lectures at Göttingen; (1860–62).
3 Math. Ann. 5.
4 Crelle J., 80.
5 C. R. 84.
6 Mem. Coll. Sci., Kyoto, 2, 255 (1917).

the remarkable memoir of Picard[1] in 1890, the method of successive approximations was applied. This method, as well as that of Cauchy, is used for the linear partial differential equations in the field of the real variables. The problem has been developed to the researches of Fredholm. On the other hand, the general problems of the partial differential equations were almost completed by Goursat in his books; especially the theory of characteristics of Cauchy. But the analytical problems of the solutions of the partial differential equations have been developed but slowly. We cite the researches of Le Roux in 1892[2] and 1898[3] and of Delassus[4] in 1895 about the linear homogeneous partial differential equations of the higher orders by aid of Picard's method. In these memoirs the singular points (lines) of the equations with two independent variables are determined and some singular solutions of Euler's equation are determined. In 1916 the thesis of Stoïlow was published which treats of the solutions of the same equations, being given the initial functions with the singular points on characteristics. In this research, Goursat's[5] note in 1906 is applied. But analytical researches into the solutions at the fixed singularities have not appeared, with the one exception of Poincaré's paper. While after Marotte[6], Darboux demonstrated that the equation

$$(x+\cdots)\frac{\partial f}{\partial x}+(\lambda_1 x_1+\cdots)\frac{\partial f}{\partial x_1}+(\lambda_2 x_2+\cdots)\frac{\partial f}{\partial x_2}=0,$$

has solutions of the form

$$u_1=\frac{(A_1x_1+\cdots)^{\frac{1}{\lambda_1}}}{Ax+\cdots}, \qquad u_2=\frac{(A_2x_2+\cdots)^{\frac{1}{\lambda_2}}}{Ax+\cdots},$$

(under certain conditions of $\lambda_1$, $\lambda_2$). On the other hand, Darboux read Poincaré's thesis[7], but he says nothing about this fact and I am not certain who was the first discoverer.

The present paper contains discussions of more general equations than those in the former two[8]; namely the equation

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1 Jordan J.; J. l'ecole poly.

2, 4 Ann. l'ecole nor. sup.

3 Jordan J.

5 Bull. Soc. Math. Fr.

6 C. R. (1896).

7 Oeuvres de Poincaré, II, xxi.

8 Mem. Coll. Sci., Kyoto., 2, (1917); 4, (1919).

$$\xi_1(x)\frac{\partial f}{\partial x_1}+\xi_2(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_n(x)\frac{\partial f}{\partial x_n}=0,$$

where $\xi_1(x)$, $\xi_2(x),\ldots\xi_n(x)$ are holomorphic about and vanish at $x_1=x_2=\cdots=x_n=0$. For this purpose I use a simple birational transformation plane to plane and the solutions are of a particular type of Laurent's expansions in a certain domain. After this, the method is extended to the discussions of the complete system.

1. Let us consider the transformation:

$$\left.\begin{aligned} x_1 &= y_1 y_n^m, \\ &\cdots\cdots\cdots\cdots \\ x_{n-1} &= y_{n-1} y_n^m, \\ x_n &= y_n, \end{aligned}\right\} \qquad (1)$$

where $m$ is a positive integer. By this transformation, for a system of values $(y_1\ldots, y_{n-1}, y_n)$ there corresponds one and only one system of values $(x_1, \ldots x_{n-1}, x_n)$ and for $y_1=\cdots=y_{n-1}=y_n=0$, $x_1=\cdots=x_{n-1}=x_n=0$. A holomorphic function $f(x)$ of the variables $x_1,\ldots x_{n-1}, x_n$ becomes also a holomorphic function of $y_1,\ldots y_{n-1}, y_n$. Next, by $P_x(R_1; \ldots; R_n)$ we mean a domain consisting of circular domains with radii $R_i$, and centres at $x_i=0$, in the plane of $x_i$ $(i=1, 2, \ldots n)$. Specially when $R_1=\cdots=R_n=R$, we express it by $P_x(R)$. If $f(x)$ be holomorphic in a domain containing $P_x(R)$, then we have an expansion in $P_x(R)$,

$$f(x)=\sum a_{p_1\cdots p_n} x_1^{p_1}\cdots x_n^{p_n},$$

then we have

$$\left| a_{p_1\cdots p_n} \right| < \frac{M}{R^{p_1+\cdots+p_n}}, \qquad (2)$$

where $M$ is the maximum modulus of the function $f(x)$ on the circles of $P_x(R)$. By the transformation (1), we have

$$f(x)=\sum a_{p_1\cdots p_{n-1}p_n} y_1^{p_1}\cdots y_{n-1}^{p_{n-1}} y_n^{m(p_1+\cdots+p_{n-1})+p_n},$$

and suppose this expansion has a common factor $y_n^m$, then writing

$$f(x)=y_n^m \varphi(y),$$

we have

$$\varphi(y)=\sum a_{p_1\cdots p_{n-1}p_n}\, y_1^{p_1}\cdots y_{n-1}^{p_{n-1}}\, y_n^{m(p_1+\cdots+p_{n-1})+p_n-m},$$

where all the powers of $y_n$ are positive integers or zero. Since the series $f(x)$ is convergent in the domain $P_x(R)$, if $R>1$, it is clear that $y_n^m\varphi(y)$ is also convergent in the domain $P_y(R^{\frac{1}{m+1}})$, but it is not *a priori* clear that $\varphi(y)$ is convergent in the domain $P_y(R^{\frac{1}{m+1}})$, though it is clear for the case of one variable. By the inequality (2), we have

$$|\varphi(y)|<\sum\frac{M}{R^{p_1+\cdots+p_{n-1}+p_n}}\left|y_1^{p_1}\cdots y_{n-1}^{p_{n-1}}\, y_n^{m(p_1+\cdots+p_{n-1})+p_n-m}\right|$$

$$=\frac{M}{\rho^m}\sum\frac{\rho^{(m+1)(p_1+\cdots+p_{n-1})+p_n}}{R^{p_1+\cdots+p_{n-1}+p_n}}\left|\frac{y_1}{\rho}\right|^{p_1}\cdots\left|\frac{y_{n-1}}{\rho}\right|^{p_{n-1}}\left|\frac{y_n}{\rho}\right|^{m(p_1+\cdots+p_{n-1})+p_n-m},$$

where $\rho$ is positive yet undetermined. If we give to $\rho$ such *a* value that the first factors in $\Sigma$ be less than unity, then we have

$$|\varphi(y)|<\frac{M}{\rho^m}\sum\left|\frac{y_1}{\rho}\right|^{p_1}\cdots\left|\frac{y_{n-1}}{\rho}\right|^{p_{n-1}}\left|\frac{y_n}{\rho}\right|^{m(p_1+\cdots+p_{n-1})+p_n-m}$$

$$<\frac{M}{\rho^m}\,\frac{1}{\left(1-\left|\frac{y_1}{\rho}\right|\right)\cdots\left(1-\left|\frac{y_{n-1}}{\rho}\right|\right)\left(1-\left|\frac{y_n}{\rho}\right|\right)}.$$

Hence $\varphi(y)$ is convergent in the domain $P_y(\rho)$. To determine $\rho$, if $R\leqq 1$, we have only to take $\rho=R$. But when $R>1$, we must determine $\rho$ such that

$$\rho^{(m+1)(p_1+\cdots+p_{n-1})+p_n}\leqq R^{p_1+\cdots+p_{n-1}+p_n}, \qquad (3)$$

for any $p_1+\cdots+p_{n-1}+p_n$. But since

$$\frac{(m+1)(p_1+\cdots+p_{n-1})+p_n}{p_1+\cdots+p_{n-1}+p_n}=m\,\frac{p_1+\cdots+p_{n-1}}{p_1+\cdots+p_{n-1}+p_n}+1\leqq m+1,$$

if we take $\rho$ such that

$$\rho=R^{\frac{1}{m+1}},$$

the above inequality (3) is satisfied Hence we have the lemma:

*Between two power-series $f(x)$ and $\varphi(y)$, by our transformation* (1) *let such a relation as*

$$f(x)=y^m\varphi(y)$$

*be established. If $f(x)$ be convergent in $P_x(R)$, then $\varphi(y)$ is convergent in $P_y(\rho)$, where*

$$\rho=R, \text{ or } \rho=R^{\frac{1}{m+1}}$$

*according as $R\leqq 1$ or $R>1$.*

2. Let us consider the inverse transformation of (1), namely

$$\left.\begin{aligned} y_1&=x_1x_n^{-m},\\ &\cdots\cdots\cdots\cdots\\ y_{n-1}&=x_{n-1}x_n^{-m},\\ y_n&=x_n. \end{aligned}\right\} \tag{4}$$

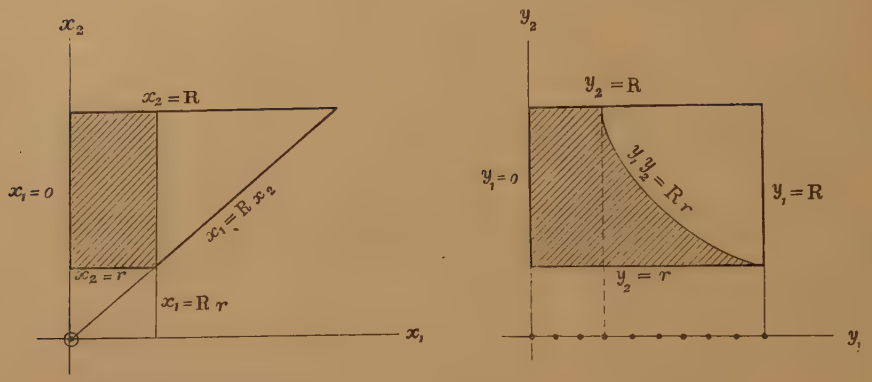
Since

$$\frac{\partial(x_1,\ldots x_n)}{\partial(y_1,\ldots y_n)}=y_n^{m(n-1)},$$

between $(x_1,\ldots x_{n-1},x_n)$ and $(y_1\ldots y_{n-1},y_n)$, there is one-one correspondence provided $y_n\neq o$. Now by $P_x(R_1;\ldots;R_{n-1};R_n,r)$, we mean a domain consisting of $n-1$ circles with radii $R_1,\ldots R_{n-1}$, with centres at the origins in the planes of $x_1,\ldots x_{n-1}$ respectively, and of two concentric circles with radii $R_n$ and $r$ $(R>r)$ and centres at the origin of the plane of $x_n$. When $R_1=\ldots=R_{n-1}=R_n=R$, we write it $P_x(R;R,r)$. Now by the transformation (4), any holomorphic function $\varphi(y)$ in the domain $P_y(R_1;\ldots;R_{n-1};R_n,r)$ will be transformed into a holomorphic function $f(x)$ in the domain $P_x(R_1r^m;\ldots;R_{n-1}r^m;R_n,r)$. When $R_1=\cdots=R_{n-1}=R_n=R$, the domain will become $P_y(R;R,r)$ and $P_x(Rr^m;R,r)$. But we do not say that these domains have one-one correspondence by our transformation. Truly the domain $P_x(Rr^m;R,r)$ is contained in the domain transformed from $P_y(R;R,r)$. An illustration with two real variables is given in the following figures.

Representation of the transformation for $m=1$:

$$\left.\begin{aligned} x_1&=y_1y_2\\ x_2&=y_2 \end{aligned}\right\} \text{ or } \left.\begin{aligned} y_1&=x_1x_2^{-1}\\ y_2&=x_2 \end{aligned}\right\}$$




Domain corresponding to $P_y$. $P_y(R; R, r)$

The shaded part of the left figure is $P_x(Rr; R, r)$ which corresponds to the shaded part of the domain $P_y(R; R, r)$ in the right figure.

The transformation (1) forms a group of one parameter $m$. Its infinitesimal transformation is given by

$$log\, x_n \cdot \left( x_1 \frac{\partial f}{\partial x_1} + \cdots + x_{n-1} \frac{\partial f}{\partial x_{n-1}} \right);$$

hence the invariants of the group are given by $\frac{x_i}{x_j} = \text{const.}$ and $x_n = \text{const.}$, where $i \neq j \neq n$. While the transformation (9) below forms a group of $n$ parameters $m, l_1 \ldots l_{n-1}$ and hence is a transitive group. The infinitesimal transformations are

$$log\, x_n \cdot \left( x_1 \frac{\partial f}{\partial x_1} + \cdots + x_{n-1} \frac{\partial f}{\partial x_{n-1}} \right),\ x_n \frac{\partial f}{\partial x_1},\ \ldots\ldots,\ x_n \frac{\partial f}{\partial x_{n-1}}.$$

We remember that in each case the point $x_n = o$ belongs to the singular points of the transformations; but excepting the point, the transformations are birational and of plane to plane.

Next we shall consider the relations between the partial derivatives with respect to the transformation (1). Let $f$ be a function of the variables $x_1 \ldots x_{n-1}, x_n$ and hence of the variables $y_1, \ldots y_{n-1}, y_n$, then we have

$$\left.\begin{aligned}
&\frac{\partial f}{\partial y_1}=y_n^m\frac{\partial f}{\partial x_1},\\
&\cdots\cdots\cdots\quad\cdots\cdots\cdots\\
&\frac{\partial f}{\partial y_{n-1}}=y_n^m\frac{\partial f}{\partial x_{m-1}},\\
&\frac{\partial f}{\partial y_n}=m\left(y_1y_n^{m-1}\frac{\partial f}{\partial x_1}+\cdots+y_{n-1}y_n^{m-1}\frac{\partial f}{\partial x_{n-1}}\right)+\frac{\partial f}{\partial x_n}.
\end{aligned}\right\}\qquad(5)$$

Multiplying the first $n-1$ equations by $y_1, \ldots y_{n-1}$ respectively, and the last by $y_n$, we have by aid of the transformation (1),

$$\left.\begin{aligned}
&y_1\frac{\partial f}{\partial y_1}=x_1\frac{\partial f}{\partial x_1},\\
&\cdots\cdots\cdots\cdots,\\
&y_{n-1}\frac{\partial f}{\partial y_{n-1}}=x_{n-1}\frac{\partial f}{\partial x_{n-1}},\\
&y_n\frac{\partial f}{\partial y_n}=m\left(y_1\frac{\partial f}{\partial y_1}+\cdots+y_{n-1}\frac{\partial f}{\partial y_{n-1}}\right)+x_n\frac{\partial f}{\partial x_n}.
\end{aligned}\right\}\qquad(5')$$

3. Now returning to our problem, consider as usual the partial differential equation

$$Xf\equiv\xi_1(x)\frac{\partial f}{\partial x_1}+\cdots+\xi_{n-1}(x)\frac{\partial f}{\partial x_{n-1}}+\xi_n(x)\frac{\partial f}{\partial x_n}=o,\qquad(6)$$

where $\xi_1(x), \ldots, \xi_{n-1}(x), \xi_n(x)$ are regular with respect to $x_1, \ldots x_{n-1}, x_n$, in the domain $P_x(R)$ and vanish at $x_1=\cdots=x_{n-1}=x_n=o$. But *we do not expect that they necessarily begin with terms of the first orders of* $x_1, \ldots x_{n-1}, x_n$.

It may occur that among the power-series $\xi_1(x), \ldots, \xi_{n-1}(x)$, there is at least one which contain such term or terms as $ax^m$, $a$ being a constant. Let $m$ be the *smallest index*, not zero, among them and be contained in $\xi_1(x)$. Applying the transformation (1), we have

$$\begin{aligned}
\xi_1(x)&=y_n^mP_1(y),\\
&\cdots\cdots\cdots\cdots\\
\xi_{n-1}(x)&=y_n^mP_{n-1}(y),\\
\xi_n(x)&=y_n^{m'}P_n(y),
\end{aligned}$$

where $P_1(y), \ldots, P_{n-1}(y), P_n(y)$ are power-series and $m'$ a positive integer and

$$P_1(o) = a \neq o.$$

By the lemma proved in § 1, these power-series are all convergent in the domain $P_y(\rho)$. Now by the relations (5) and (5′), we have

$$\begin{aligned} Xf = {} & P_1(y)\frac{\partial f}{\partial y_1} + \cdots + P_{n-1}(y)\frac{\partial f}{\partial y_{n-1}} \\ & + y_n^{m'} P_n(y)\frac{\partial f}{\partial y_n} - m y_n^{m'-1} P_n(y)\left(y_1 \frac{\partial f}{\partial y_1} + \cdots + y_{n-1}\frac{\partial f}{\partial y_{n-1}}\right) \\ = {} & \left\{P_1(y) - m y_1 y_n^{m'-1} P_n(y)\right\}\frac{\partial f}{\partial y_1} + \cdots + \left\{P_{n-1}(y) - m y_{n-1} y_n^{m'-1} P_n(y)\right\}\frac{\partial f}{\partial y_{n-1}} \\ & + y_n^{m'} P_n(y)\frac{\partial f}{\partial y_n}, \end{aligned}$$

where, of course, at the point $y_1 = \cdots = y_{n-1} = y_n = o$,

$$P_1(y) - m y_1 y_n^{m'-1} P_n(y) = a \neq o..$$

Hence our equation (6), divided by the first coefficient, will be transformed into the following

$$Yf \equiv \frac{\partial f}{\partial y_1} + \eta_2(y)\frac{\partial f}{\partial y_2} + \cdots + \eta_n(y)\frac{\partial f}{\partial y_n} = o, \tag{7}$$

where $\eta_2(y), \ldots, \eta_n(y)$ are holomorphic in a certain domain contained in $P_y(\rho)$.

4. When no one of the series $\xi_1(x), \ldots, \xi_{n-1}(x)$ contains such a term as $a x_n^m$, we take another variable *e.g.* $x_i$ instead of $x_n$ and the same process may be followed. But if all these cases fail, we consider the transformation:

$$\left.\begin{aligned} x_1 &= y_1 + l_1 y_n, \\ &\cdots\cdots\cdots\cdots, \\ x_{n-1} &= y_{n-1} + l_{n-1} y_n, \\ x_n &= y_n, \end{aligned}\right\} \tag{8}$$

where $l_1, \ldots l_{n-1}$ are constants, at least one of which is not zero. The inverse transformation is clearly

$$\left.\begin{aligned} y_1 &= x_1 - l_1 x_n, \\ &\cdots\cdots\cdots\cdots, \\ y_{n-1} &= x_{n-1} - l_{n-1} x_n, \\ y_n &= x_n, \end{aligned}\right\}$$

and hence between $(x_1, \ldots x_{n-1}, x_n)$ and $(y_1, \ldots y_{n-1}, y_n)$ there is one-one correspondence in all extents of the variables. By this transformation the equation (6) will become

$$Xf = \left\{\xi_1(x) - l_1\xi_n(x)\right\}\frac{\partial f}{\partial y_1} + \cdots + \left\{\xi_{n-1}(x) - l_{n-1}\xi_n(x)\right\}\frac{\partial f}{\partial y_{n-1}} + \xi_n(x)\frac{\partial f}{\partial y_n} = o.$$

In the first $n-1$ coefficients of this equation expressed in terms of $y_1, \ldots y_{n-1}, y_n$, there must occur at least such a term as $ay_n^m$. Consequently we may proceed with the new equation just as before. In any case, by the composition of the transformations (1) and (8), namely, *by the transformation*

$$\left.\begin{aligned} x_1 &= y_1 y_n^m + l_1 y_n, \\ &\cdots\cdots\cdots\cdots, \\ x_{n-1} &= y_{n-1} y_n^m + l_{n-1} y_n, \\ x_n &= y_n, \end{aligned}\right\} \qquad (9)$$

*the equation* (6) *will be transformed into the equation* (7). Therefore we assume, without loosing the generality, $l_1 = \ldots = l_{n-1} = o$.

5. The equation (7) may be solved by the general method at once. Let $\varphi_1(y), \ldots, \varphi_{n-1}(y)$ be the $n-1$ first integrals, then any arbitrary function

$$F(\varphi_1(y), \ldots, \varphi_{n-1}(y))$$

is the general integral of the equation (7), the functions $\varphi_1(y), \ldots \varphi_{n-1}(y)$ being regular about the point $y_1 = \cdots = y_{n-1} = y_n = o$. Let $P_y(R; R, r)$ be the corresponding domain. By the transformation (4) the equation (7) is transformed into (6), while the first integrals $\varphi_1(y), \ldots, \varphi_{n-1}(y)$ will become $f_1(x), \ldots, f_{n-1}(x)$ which are the $n-1$ first integrals of the equation (6), and $F(f_1(x), \ldots, f_{n-1}(x))$ is the required general integral of the equation (6). By aid of § 2 the integrals $f_1(x), \ldots, f_{n-1}(x)$ are holomorphic in the domain $P_x(Rr^m; R, r)$ and truly they are expanded into the Laurent-series. Thus we have the theorem:

*The partial differential equation*

$$Xf=\xi_1(x)\frac{\partial f}{\partial x_1}+\cdots+\xi_{n-1}(x)\frac{\partial f}{\partial x_{n-1}}+\xi_n(x)\frac{\partial f}{\partial x_n}=o,$$

*where* $\xi_1(x), \ldots, \xi_{n-1}(x), \xi_n(x)$ *are regular analytic about the point* $x_1=\ldots=x_{n-1}=x_n=o$, *at which they vanish simultaneously, has the general integral*

$$F(f_1(x), \ldots, f_{n-1}(x));$$

$f_1(x), \ldots, f_{n-1}(x)$ *are* $n-1$ *first integrals and have the form of the* Laurent-series *in such a domain as* $P_x(Rr^m; R, r)$.

6. It is not necessary to take the convergent circles of $\eta_2(y), \ldots \eta_n(y)$ to have the same radii $R$, and consequently the wider domain $P_x(R_1r^m; \ldots; R_{n-1}r^m; R_n, r)$ may be taken for the domain of the integrals $f_1(x), \ldots, f_{n-1}(x)$. This domain has a particular property. Since

$$R_ir^m, \ (i=1, \ldots, n-1)$$

vanish at $r=o$, though we make the variable $x_n$ an infinitesimal of the first order, yet the integrals $f_1(x), \ldots, f_{n-1}(x)$ remain finite and determinate, provided the orders of the infinitesimals of the other variables $x_1, \ldots x_{n-1}$ be not lower than $m$. We may extend the domain further by Goursat's theorem[1]. The first integrals $\varphi_1(y), \ldots, \varphi_{n-1}(y)$ are power-series. But if we use his theorem, they are holomorphic in a somewhat wider domain. Consequently the transformed functions $f_1(x), \ldots, f_{n-1}(x)$ will become holomorphic in a somewhat wider domain than $P_x(R_1r^m; \ldots; R_{n-1}r^m; R, r)$.

7. We have assumed that in § 4, $l_1, \ldots l_{n-1}$ are all zero, since by the transformation (8) the differential expression $Xf$ becomes

$$Xf=\left\{\xi_1(x)-l_1\xi_n(x)\right\}\frac{\partial f}{\partial y_1}+\cdots+\left\{\xi_{n-1}(x)-l_{n-1}\xi_n(x)\right\}\frac{\partial f}{\partial y_{n-1}}+\xi_n(x)\frac{\partial f}{\partial y_n},$$

on which in general we may apply the transformation (1). But for a special case, it may occur that the transformed expression remains unchanged. In this case our method cannot be applied. Now under the assumption, we have at first

$$\xi_n(y_1+l_1y_n, \ldots, y_{n-1}+l_{n-1}y_n, y_n)=\xi_n(y_1, \ldots, y_{n-1}, y_n). \qquad (10)$$

[1] Bull. Soc. Math. Fr. (1906).

Next we have

$$\xi_i(y_1+l_1y_n, \cdots, y_{n-1}+l_{n-1}y_n, y_n)-l_i\xi_n(y_1+l_1y_n, \cdots, y_{n-1}+l_{n-1}y_n, y_n)$$
$$=\xi_i(y_1, \cdots, y_{n-1}, y_n).$$

Hence by aid of (10),

$$\xi_i(y_1+l_1y_n, \cdots, y_{n-1}+l_{n-1}y_n, y_n)-\xi_i(y_1, \cdots, y_{n-1}, y_n)$$
$$=l_i\xi_n(y_1, \cdots, y_{n-1}, y_n). \tag{11}$$

Therefore we have

$$\xi_i(y_1+2l_1y_n, \cdots, y_{n-1}+2l_{n-1}y_n, y_n)-\xi_i(y_1+l_1y_n, \cdots, y_{n-1}+l_{n-1}y_n, y_n)$$
$$=l_i\xi_n(y_1, \cdots, y_{n-1}, y_n).$$

Hence we have by equating the left-hand sides

$$\xi_i(y_1+2l_1y_n, \cdots, y_{n-1}+2l_{n-1}y_n, y_n)+\xi_i(y_1, \cdots, y_{n-1}, y_n)$$
$$=2\xi_i(y_1+l_1y_n, \cdots, y_{n-1}+l_{n-1}y_n, y_n).$$

This equation being identical with respect to $l_1, \cdots l_{n-1}$ we must have, expanding both sides into Taylor's series, the relations

$$\frac{\partial^2\xi_i(y)}{\partial y_h\partial y_k}=o, \qquad \begin{matrix}h\\k\end{matrix}=1, \cdots, n-1.$$

So that we have

$$\xi_i(y)=A_{i1}(y_n)y_1+\cdots+A_{in-1}(y_n)y_{n-1}+A_i(y_n).$$

But since $\xi_i(y)$ vanishes for $y_1=\cdots=y_{n-1}=y_n=o$, we have rather

$$\xi_i(y)=A_{i1}(y_n)y_1+\cdots+A_{in-1}(y_n)y_{n-1}+A_{in}(y_n)y_n, \quad i=1, \cdots n-1,$$

where $A_{i1}(y_n), \cdots A_{in-1}(y_n), A_{in}(y_n)$ are regular with respect to $y_n$. Substituting this expression in (11),

$$\sum_{j=1}^{n-1}A_{ij}(y_n)l_jy_n=l_i\xi_n(y_1, \cdots, y_{n-1}, y_n).$$

Hence we have

$$A_{ii}(y_n)=\frac{\xi_n(y)}{y_n}\equiv M(y), \qquad i, j=1, 2, \cdots n-1,$$
$$A_{ij}(y_n)=o, \qquad i\neq j,$$

that is

$$\xi_i(y)=y_iM(y), \qquad i=1, 2, \cdots n.$$

Our differential expression is therefore

$$Xf=M(x)\left(x_1\frac{\partial f}{\partial x_1}+\cdots+x_{n-1}\frac{\partial f}{\partial x_{n-1}}+x_n\frac{\partial f}{\partial x_n}\right).$$

In this case the first integrals can at once be found or we may consider a little more complex transformation than (8).

We shall make a remark upon this equation. Suppose $M(x)=1$, then consider the equation

$$x_1\frac{\partial f}{\partial x_1}+\cdots+x_{n-1}\frac{\partial f}{\partial x_{n-1}}+x_n\frac{\partial f}{\partial x_n}=\lambda f.$$

This equation shows that the function $f$ is homogeneous of the $\lambda$th order with respect to the variables. Especially the equation

$$x\frac{\partial f}{\partial x}+y\frac{\partial f}{\partial y}+z\frac{\partial f}{\partial z}=-2f$$

is satisfied by Weierstrass' $\wp$-function with two periods $x$ and $y$. This function is uniform about the point $x=y=z=o$.

8. We proceed to the problem of a complete system of partial differential equations. This case may partly be solved by a method similar to that by which I succeeded before as shown in the first paper[1].

Let a complete system

$$\left.\begin{aligned}
&X_1f\equiv\xi_{11}(x)\frac{\partial f}{\partial x_1}+\xi_{12}(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_{1n}(x)\frac{\partial f}{\partial x_n}=o,\\
&X_2f\equiv\xi_{21}(x)\frac{\partial f}{\partial x_1}+\xi_{22}(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_{2n}(x)\frac{\partial f}{\partial x_n}=o,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&X_rf\equiv\xi_{r1}(x)\frac{\partial f}{\partial x_1}+\xi_{r2}(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_{rn}(x)\frac{\partial f}{\partial x_n}=o,
\end{aligned}\right\}\qquad(12)$$

be given, where $r<n$, and $\xi_{11}(x), \xi_{12}(x), \ldots, \xi_{rn}(x)$ are regular about and vanish at the point $x_1=x_2=\cdots=x_n=o$ and among $X_1f, X_2f, \ldots, X_rf$, we have the relations

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[1] loc. cit. (1917).

$$(X_iX_j)f=\sum_{s=1}^{r} C_{ijs}X_sf, \qquad i,j=1,2,\ldots\ldots r.$$

We *assume* that all the functions $C_{ijs}$ are holomorphic about the point $x_1=x_2=\ldots x_n=o$. Among $\xi_{i1}(x)$, $\xi_{i2}(x)$, ..., $\xi_{in-1}(x)$, $(i=1,2,\ldots r)$, let $\xi_{11}(x)$ be one which contains such terms as $ax_n^m$ where $m$ is the smallest positive integer. [If this assumption be absurd, we have only to consider the transformation (8)]. Then applying the transformation (1), we have the following complete system

$$\left.\begin{aligned}
&Y_1f\equiv\frac{\partial f}{\partial y_1}+\eta_{12}(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_{1n}(y)\frac{\partial f}{\partial y_n}=o,\\
&Y_2f\equiv\eta_{21}(y)\frac{\partial f}{\partial y_1}+\eta_{22}(\eta)\frac{\partial f}{\partial y_2}+\cdots+\eta_{2n}(y)\frac{\partial f}{\partial y_n}=o,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&Y_rf\equiv\eta_{r1}(y)\frac{\partial f}{\partial y_1}+\eta_{r2}(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_{rn}(y)\frac{\partial f}{\partial y_n}=o,
\end{aligned}\right\} \qquad (13)$$

where all the coefficients $\eta_{12}(y)$, $\ldots\eta_{1n}(y)$, $\ldots\eta_{rn}(y)$ are holomorphic about the point $y_1=y_2=\cdots=y_n=o$, and such that

$$(Y_iY_j)f=\sum_{s=1}^{r} D_{ijs}Y_sf, \qquad i,j=1,2,\ldots\ldots r.$$

It can easily be shown that all the functions $D_{ijs}$ are also holomorphic about the point $y_1=y_2=\cdots=y_n=o$.
Now put

$$Y_i'f\equiv Y_if+\sum_{j=1}^{r} R_{ij}(y)Y_jf,$$

where $R_{ij}(y)$, $(j=1,2,\ldots r)$ are yet unknown functions; then for the permutability of the infinitesimal transformations $Y_1f$ and $Y_i'f$, we must have these functions such that

$$Y_1R_{is}+D_{1is}+\sum_{j=1}^{r} D_{1js}R_{ij}=o, \qquad s=1,2,\ldots\ldots r.^{1}$$

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1 See the first Memoir (pp. 290—1).

But this is a system of $r$ simultaneous partial differential equations of the first order with respect to the unknowns $R_{ij}$, $(j=1, 2,...r)$. All the coefficients are holomorphic about the point $x_1=x_2=\cdots=x_n=o$ and those of $\dfrac{\partial R_{is}}{\partial y_1}$, $(s=1, 2,...r)$ are unity. Hence by the general theorem, with respect to the ordinary points, there exists a system of holomorphic solutions $R_{is}(y)$, $(s=1, 2,...r)$ about the point $x_1=x_2=\cdots=x_n=o$, with the mere initial conditions that all these functions vanish at the point $y_1=y_2=\cdots=y_n=o$. Following this process we obtain a complete system

$$Y_1'f\equiv Y_1f,\ Y_2'f,\ \ldots\ldots,\ Y_r'f, \tag{14}$$

such that

$$\begin{aligned}&(Y_1'Y_i')f\equiv o, && i, j=2, 3,\ldots\ldots r,\\ &(Y_i'Y_j')f\equiv\sum_{s=1}^{r}D'_{ijs}Y_s'f,\end{aligned} \tag{15}$$

where all the composition-functions such as $D'_{ijs}$ are holomorphic about the point $y_1=y_2=\cdots=y_n=o$. Moreover we may conclude that

$$Y_1D'_{ijt}=o,\quad i,j=2,\ldots\ldots r,\ t=1, 2,\ldots\ldots r. \tag{16}$$

9. Consider the equation

$$Y_1'f=\frac{\partial f}{\partial y_1}+\eta_{12}(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_{1n}(y)\frac{\partial f}{\partial y_n}=o.$$

By the general existence-theorem, we can find $n-1$ first integrals $\varphi_1(y),\ldots\varphi_{n-1}(y)$ which are regular about the point $y_1=y_2=\ldots=y_n=o$, satisfying the initial conditions

$$\begin{aligned}&\varphi_1(y)=y_2+\cdots\cdots,\\ &\cdots\cdots\cdots\cdots\cdots,\\ &\varphi_{n-1}(y)=y_n+\cdots\cdots,\end{aligned}$$

at $y_1=o$. The dotted parts stand for terms of higher degrees with respect to the variables $y_2,\ldots y_n$, (or we may give up these terms). Let us consider the transformation

$$\left.\begin{aligned}&z_1=y_1,\\ &z_2=\varphi_1(y)=y_2+\cdots\cdots,\\ &\cdots\cdots\cdots\cdots\cdots,\\ &z_n=\varphi_{n-1}(y)=y_n+\cdots\cdots,\end{aligned}\right\} \tag{17}$$

the dotted parts stand for terms of higher degrees with respect to the variables $y_1, y_2, \cdots y_n$. This transformation is reversibly holomorphic about the point $y_1=y_2=\cdots=y_n=o$. Applying this to the complete system (14), then we obtain a system such as

$$1^\circ. \qquad Z_1 f \equiv \frac{\partial f}{\partial z_1},$$

$$Z_2 f \equiv \zeta_{21}(z)\frac{\partial f}{\partial z_1} + \zeta_{22}(z)\frac{\partial f}{\partial z_2} + \cdots + \zeta_{2n}(z)\frac{\partial f}{\partial z_n},$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots,$$

$$Z_r f \equiv \zeta_{r1}(z)\frac{\partial f}{\partial z_1} + \zeta_{r2}(z)\frac{\partial f}{\partial z_2} + \cdots + \zeta_{rn}(z)\frac{\partial f}{\partial z_n},$$

where the coefficients $\zeta_{21}(z), \zeta_{22}(z), \ldots, \zeta_{rn}(z)$ are holomorphic about the point $z_1=z_2=\cdots=z_n=o$ By aid of (15), these differential expressions satisfy the relations

$$2^\circ. \qquad (Z_1 Z_i) f \equiv o,$$

$$3^\circ. \qquad (Z_i Z_j) f \equiv \sum_{s=1}^{r} E_{ijs} Z_s f, \qquad i, j = 2, \ldots\ldots r,$$

where all the composition-functions $E_{ijs}$ are holomorphic about the point $z_1=z_2=\cdots=z_n=o$. Now by aid of $2^\circ$ we have

$$Z_1 \zeta_{is} \equiv o, \qquad i = 2, \ldots\ldots r, \quad s = 1, 2, \ldots\ldots n,$$

and by (16) we have

$$Z_1 E_{ijt} \equiv o, \qquad i, j = 2, \ldots\ldots r, \quad t = 1, 2, \ldots\ldots r.$$

These results mean that all the functions $\zeta_{is}(z)$ and $E_{ijt}$ are independent of the variable $z_1$. Now put

$$\bar{Z}_i f \equiv Z_i f - \zeta_{i1}(z) Z_1 f \qquad (18)$$

$$= \zeta_{i2}(z)\frac{\partial f}{\partial z_2} + \cdots + \zeta_{in}(z)\frac{\partial f}{\partial z_n}, \qquad i = 2, \ldots\ldots r.$$

Then still we have

$$(Z_1 \bar{Z}_i) f \equiv o, \qquad i = 2, \ldots\ldots r.$$

Moreover we have

$$(\bar{Z}_i\bar{Z}_j)f\equiv\sum_{s=1}^{r}E_{ijs}\bar{Z}_sf, \qquad i,j=2,\ldots\ldots r.$$

The newly deduced complete system consisting of $r-1$ equations with respect to $n-1$ independent variables:

$$\left.\begin{aligned}&\bar{Z}_2f\equiv\zeta_{22}(z)\frac{\partial f}{\partial z_2}+\cdots+\zeta_{2n}(z)\frac{\partial f}{\partial z_n}=0,\\&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots,\\&\bar{Z}_rf\equiv\zeta_{r2}(z)\frac{\partial f}{\partial z_2}+\cdots+\zeta_{rn}(z)\frac{\partial f}{\partial z_n}=0\end{aligned}\right\}\qquad(19)$$

may be treated in a similar way. (It may occur that among the coefficients $\zeta_{22}(z),\ldots,\zeta_{rn}(z)$, some number may exist which does not vanish at the point $z_2=\cdots=z_n=0$. In this case the next transformation of the variables is unnecessary.) Therefore, by mathematical induction we arrive at the result: *The $n-r$ integrals of the complete system of the partial differential equations* (12) *at the singular point $x_1=x_2=\cdots=x_n=0$, can be obtained by aid of some number of successively combined applications of the transformations such as* (1) *and* (17). *The forms of the integrals about the point $x_1=x_2=\cdots=x_n=0$ are very complex, but they are* uniform *in the domain surrounding the point $x_1=x_2=\cdots=x_n=0$,* (the point being excluded).

In the preceding discussions the complete system (12) is supposed as any of the coefficients $\xi_{11}(x),\xi_{12}(x),\ldots,\xi_{rn}(x)$ were not zero. But as we can easily verify, this restriction is not essential.

10. In § 9, we have used the solutions of the equation of the form

$$Yf=\frac{\partial f}{\partial y_1}+\eta_2(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_n(y)\frac{\partial f}{\partial y_n}=0,$$

having been given that initially the solutions shall become the given functions for $y_1=0$. The given functions being regular about the point $y_2=\cdots=y_n=0$ and the integrals are also regular. Now for simplicity let an initial function be $y_2$ for $y_1=0$; this function will become by the transformation (1) $x_2x_n^{-m}$. For this function, the point $x_1=x_2=\cdots=x_n=0$ is an unessential singularity. Therefore by our transformation, we can find such a solution as will become $x_2x_n^{-m}$ for $x_1=0$ of the equation:

$$Xf\equiv\xi_1(x)\frac{\partial f}{\partial x_1}+\xi_2(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_n(x)\frac{\partial f}{\partial x_n}=0$$

in the domain $P_x(Rr^m; R, r)$.

The general problem of the integral at the singular point, being given initially a function with singularity at a point, is very difficult. But when the singular point $x_1=x_2=\cdots=x_n=o$ be an unessential singularity of the given function, *i.e.*, when we may write it

$$\frac{P(x)}{Q(x)},$$

where $P(x)$ and $Q(x)$ are regular about and vanish at the point $x_1=x_2=\cdots=x_n=o$, by our transformation (1), if this function become regular about the point, we can also find the solution of the equation $Xf=o$ with this initial function. This property may be extended to such an equation as

$$Xf=F(x, f)\equiv u(x)f+v(x),$$

where $u(x)$ and $v(x)$ are holomorphic about the point $x_1=x_2=\cdots=x_n=o$. When the functions $\xi_1(x), \xi_2(x), \ldots, \xi_n(x)$; $u(x), v(x)$ have the point $x_1=x_2=\cdots=x_n=o$ as an unessential singularity, our method may still be applied; for by the multiplication of a certain regular function of $x_1, x_2, \ldots x_n$ into the equation, it should be transformed into the form already discussed. But such function, equated to zero, is nothing but the singular manifoldness which is fixed. Thus *our method may be applied to the fixed singularity of the higher class.* For the homogeneous partial differential equation of the *higher order*, Mr. Stoïlow found singular solutions at the moving singularity, the initial function being quasi-uniform, but not at the fixed singularity.

11. After this extension we can easily give up the assumption made in § 8. We have assumed that all the composition-functions $C_{ijs}$ were holomorphic about the point $x_1=x_2=\cdots=x_n=o$. We shall first prove that these functions, if not holomorphic, must have only an *unessential* singularity. From the relations

$$(X_iX_j)f=\sum_{s=1}^{n}(X_i\xi_{js}-X_j\xi_{is})\frac{\partial f}{\partial x_s}$$

$$=\sum_{t=1}^{r}C_{ijt}X_tf$$

$$=\sum_{s=1}^{n}\sum_{t=1}^{r}C_{ijt}\xi_{ts}\frac{\partial f}{\partial x_s}, \qquad i, j=1, 2, \ldots\ldots r,$$

we have

$$\left.\begin{aligned} X_i\xi_{j1}-X_j\xi_{i1}&=C_{ij1}\xi_{11}+C_{ij2}\xi_{21}+\cdots+C_{ijr}\xi_{r1},\\ X_i\xi_{j2}-X_j\xi_{i2}&=C_{ij1}\xi_{12}+C_{ij2}\xi_{22}+\cdots+C_{ijr}\xi_{r2},\\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots,\\ X_i\xi_{jn}-X_j\xi_{in}&=C_{ij1}\xi_{1n}+C_{ij2}\xi_{2n}+\cdots+C_{ijr}\xi_{rn},\end{aligned}\right\} \qquad (20)$$

$$i,\ j=1,\ 2,\ldots\ldots r.$$

Since $X_1f, X_2f,\ldots X_rf$ are linearly independent, we may assume without loosing the generality that

$$\Delta_{ij}(x)\equiv\begin{vmatrix}\xi_{11} & \xi_{12} & \cdots\cdots & \xi_{1r}\\ \xi_{21} & \xi_{22} & \cdots\cdots & \xi_{2r}\\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots\\ \xi_{r1} & \xi_{r2} & \cdots\cdots & \xi_{rr}\end{vmatrix}\not\equiv o.$$

Therefore from the first $r$ equations of (20), we can find all the functions $C_{ij1}, C_{ij2},\ldots C_{ijr}$. The functions $\xi_{11}(x), \xi_{12}(x),\ldots, \xi_{rn}(x)$ being all holomorphic about the point $x_1=x_2=\cdots=x_n=o$, we see that all the functions $C_{ij1}, C_{ij2}, C_{ijr}$ may have only unessential singularities. But if the point $x_1=x_2=\cdots=x_n=o$ belong to the unessential singularity, then we put $\Delta(x)$ the least common multiple of all the functions $\Delta_{ij}(x)$ and

$$\Delta(x)X_if\equiv\bar{X}_if, \qquad i=1,\ 2,\ldots\ldots r,$$

so that

$$(\bar{X}_i\bar{X}_j)f=(\Delta X_i,\ \Delta X_j)f$$

$$=X_i\Delta\bar{X}_jf-X_j\Delta\bar{X}_if+\sum_{s=1}^{r}\Delta C_{ijs}\bar{X}_sf$$

Sinee all the products $\Delta C_{ijs}$ are regular, $\bar{X}_1f, \bar{X}_2f,\ldots\bar{X}_rf$ constructs a complete system whose composition-functions are all regular about the point $x_1=x_2=\cdots=x_n=o$. With this system we may go as shown in §§ 8, 9 and arrive at the same result. Thus *the discussion of the complete system of the partial differential equations is completed.*

12. In the following we shall give some applications of the preceding theory to a class of linear homogeneous partial differential equations of the second order.

Let

$$\left.\begin{aligned} Xf &\equiv \xi_1(x)\frac{\partial f}{\partial x_1}+\xi_2(x)\frac{\partial f}{\partial x_r}+\cdots+\xi_n(x)\frac{\partial f}{\partial x_n}, \\ X'f &\equiv \xi_1'(x)\frac{\partial f}{\partial x_1}+\xi_2'(x)\frac{\partial f}{\partial x_2}+\cdots+\xi_n'(x)\frac{\partial f}{\partial x_n}, \end{aligned}\right\} \quad (21)$$

where $\xi_1(x), \ldots, \xi_n(x), \ldots \xi_n'(x)$ are holomorphic about and vanish at the point $x_1=x_2=\cdots=x_n=o$. Moreover suppose that among the expansions of $\xi_1(x), \ldots, \xi_{n-1}(x)$; $\xi_1(x)$ contains such a term as $ax_n^m$ where $m$ is a least positive integer and it be the same for $\xi_1'(x)$. We consider the following linear homogenous partial differential equation of the second order:

$$\begin{aligned} X'Xf=&\left\{\xi_1'(x)\frac{\partial}{\partial x_1}+\xi_2'(x)\frac{\partial}{\partial x_2}+\cdots+\xi_n'(x)\frac{\partial}{\partial x_n}\right\}\left\{\xi_1(x)\frac{\partial}{\partial x_1}\right. \\ &\left.+\xi_2(x)\frac{\partial}{\partial x_r}+\cdots+\xi_n(x)\frac{\partial}{\partial x_n}\right\}f=u(x)f+u'(x) \end{aligned} \quad (22)$$

where $u(x)$ and $u'(x)$ are holomorphic about the point $x_1=x_2=\cdots=x_n=o$ which is a fixed singularity of the equatlon. This equation is equivalent to the linear simultaneous equations:

$$\left.\begin{aligned} Xf&=\varphi, \\ X'\varphi&=u(x)f+u'(x). \end{aligned}\right\}$$

Applying our transformation (1), this system is transformed into

$$\left.\begin{aligned} Yf &\equiv \eta_1(y)\frac{\partial f}{\partial y_1}+\eta_2(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_n(y)\frac{\partial f}{\partial y_n}=\varphi, \\ Y'f &\equiv \eta_1'(y)\frac{\partial f}{\partial y_1}+\eta_2'(y)\frac{\partial f}{\partial y_2}+\cdots+\eta_n'(y)\frac{\partial f}{\partial y_n}=v(y)f+v'(y), \end{aligned}\right\}$$

where all the functions $\eta_i(y), \eta_i'(y)$ and $v(y), v'(y)$ are regular about the point $y_1=y_2=\cdots=y_n=o$ and $\eta_1(y), \eta_1'(y)$ do not vanish at the point. The equation (22) then becomes

$$Y'Yf=v(y)f+v'(y).$$

The coefficient $\eta_1(y)\eta_1'(y)$ of $\dfrac{\partial^2 f}{\partial y_1^2}$ does not vanish at the point $y_1=y_2=\cdots=y_n=o$. Therefore, by the general theorem of the existence

of Cauchy-Kowalewski, we may prove the existence of the singular solution as will become, for $y_1=o$

$$f=\text{regular function of } y_2,\cdots y_n,$$

$$\frac{\partial f}{\partial y_1}= \quad \text{"} \quad .$$

Thus our equation (22) has solutions expanded into a special Laurent-series. These considerations may be extended further, the point $x_1=x_2=\cdots=x_n=o$ being a fixed singularity of each characteristic function of the partial differential equation.